Departamento de Ingeniería
Química y Tecnologías
del Medio Ambiente
Universidad Zaragoza

CIENCIAS
ZARAGOZA

Development of Polymer-based Nanocomposite Films with Electrical Properties based on Silver Nanowires

Final Master Project

Master Degree in Nanostructured Materials for Nanotechnology Applications

Author: Iván Moreno Vidorreta
Tutor: Silvia Irusta Alderete
Tutor: Nuria Navascués García
February 2012

INDEX

1 INTRODUCTION

This project is in line with the investigation of nanocomposite carried out by the Nanostructured Films and Particles group (NFP), which belong to the Chemical and Environmental Engineering Department of the University of Zaragoza and to the Institute of Nanoscience of Aragon. This project consists in the synthesis of silver nanowires and the subsequent preparation of nanocomposite. The final purpose of the project is obtaining an electrical conductive polymeric nanocomposite based in conductive silver nanowires.

Nanowires that were defined as having at least two dimensions at the nano-scale have received a great interest due to their optical, electrical, magnetic and thermal properties. These properties are due to its dimensionality and size confinement and the intrinsic properties of nanowires are mainly determined by its size and composition. In order to obtain these properties, it is a crucial task to synthesize size-controlled nanowires.

The synthesis of silver (Ag) nanowires is an area of active research due to the high electrical and thermal conductivities of bulk silver, which is the metal with the highest conductivity in nature. In the past ten years, owing to the efforts from many research groups, some strategies were developed for the synthesis of Ag nanowires[1-4].

The synthesis strategies can be classified in two groups: the vapour phase approaches and the liquid phase approaches. Vapour phase corresponds to physical techniques such as an electronic-beam. Liquid phase synthesis is the most used methods and corresponds to chemical techniques. The homogeneous nature, the wide range of solvents, the simple monitoring technology and the low cost characterize the liquid phase processes.

Development of silver nanowires has a special significance in many applications, because its optical properties. In addition, silver nanowires are excellent conductor of electrons and photons that provides the potential for electro-optical devices. Due to its high conductivity, they are promising materials as for ultra large-scale circuits and quantum components.

Polymer matrix based nanocomposites have become a prominent area of research and development. There is large number of areas of current and emerging interest in this materials due their barrier properties, flammability resistance, biomedical applications, electrical/electronic applications, cosmetic applications and fuel cells interests [5].

Transparent conductive thin films are widely used in electronic devices, such as touch screen panel, solar cell, thin film transistors and field emission displays [6]. Conductive polymers nanocomposites possess metal-like electrical property and polymeric properties such as flexibility, low density and ease structural modification and could be obtained by dispersing conductive nanofillers such as metals or carbon based materials into insulating polymers matrices. One dimensional nanostructures materials, such as nanotubes, nanorods and nanofibers have received much research interest for nanocomposite materials. Even though silver nanowires are particularly interesting as

filler because of the properties mentioned before, there are very few publications dealing with AgNW as fillers of polymeric matrices [7,8].

The main objective of this project is the development of electrical conductive transparent polycarbonate films using silver nanowires as filler. In order to achieve this main goal the following partial objectives were pursue:

- Development of high yield (nanowire/nanoparticles ratio) synthesis of silver nanowires changing the different parameters of the synthesis.

- Development of polycarbonate film preparation method testing different methodologies and solvents.

- Obtaining a polycarbonate based composite with high conductivity and low silver nanowires load.

2 BACKGROUND

In this section, a brief summary of the basic concepts will be explained: composites, nano-composites, synthesis of nano-composites, casting technology, silver nanowires (filler), polycarbonate (matrix) and electrical theory.

2.1 Composites

A composite is form by two or more individual materials. The design goal of a composite is to achieve a combination of properties that is not displayed by any single material, and also to incorporate the best characteristics of each of the component materials. There are some natural composites but the most investigated are the synthetic ones. Composites are created to obtain a certain mechanical chemical and physical properties that correspond with the application.

Usually, composites are made of just two phases, "matrix" which is continuous and surrounds the other phase, often called "filler" or dispersed phase. The properties of composites depend on different parameters like the properties of the matrix and the filler, the relative amounts and the geometry of the dispersed phase among others [9].

2.2 Nano-composites

Nano-composite material is a composite where one of the phases has dimensions of nanometers or structures having nano-scale repeat distances between different phases [10].

Commonly, the phase that has the nanometer scale is the "filler". These nano-composites differ from conventional composite materials due to the exceptionally high surface area to volume of the filler and its exceptionally high aspect ratio, in the case of nanowires or nanolayers. Another goal of nano-composite is the yield of the filler, namely with a relatively small amount of nano-scale material an important effect on the macro-scale properties can be observed. The percentage by weight (mass fraction) of the filler introduced can remain very low (between 0,05% and 5%) due to the low filler percolation threshold.

Fillers can be classified in nano-particles (three nano-scale dimensions) as metal inorganic nano-particles, nano-fibbers (two nano-scale dimensions) as carbon nanotubes and metal inorganic wires, and nano-sheets (one nano-scale dimension) as exfoliated clays. Depend on the type of filler used, nano-composite obtain different types of properties like electrical conductivity[11], thermal conductivity[7], optical properties, dielectric properties, heat resistance[12], bactericidal properties[13] or mechanical properties (stiffness, strength and resistance to wear)[14].

2.3 Synthesis of nano-composites

Nowadays, the improvement of importance of composites has led to search of different methods to create these materials. The different methods can be classified in the following list:

- **Extrusion:** Based on moulding of a viscous thermoplastic under pressure. The polymer is added in solid state with the filler, this mixture is heated and blended using a mechanical screw that compact, melt and form a continuous charge of viscous fluid. Extrusion takes place as this molten mass is forced through a die orifice to obtain the required geometry.

- **In-situ polymerization:** In this method the polymer is polymerized in-situ in order to obtain a better interaction between the filler and the polymer. The filler is dispersed in monomer solution. This dispersion is initiated and the nano-composite material is produce.

- **Casting:** The filler is dispersed in an organic solvent and the polymer is dissolved in the same solvent. Then, these solutions are mixed and then the solvent is evaporated to obtain the bulk nano-composite. The requirements for this technique are that the polymer must be soluble in a volatile solvent and a stable solution should be formed[15].

2.4 Casting technology for nanocomposite films

Casting technique is an oldest technology for the plastic films manufacture that can be scalable to the industry. This process started to be developed due the requirement of the industry to produce large amount of polymeric uniform films[16]. The technique is widely used in the industry because the process can be adapted to a continuous manufacturing.

Casting technology has been used in recent years for many applications in order to fabricate photographic films for cameras, liquid crystal displays, print lamination, graphic arts, windows in food stuff boxes, photographical sleeves, goggles and visors.

The main advantage of solvent cast is that it not implies thermal or mechanical stress since it consists in a unique process of drying a liquid from a surface. In addition, there are more advantages of this technique: Homogeneous thickness, high optical purity and excellent transparency.

The only disadvantage is that this technique is more expensive than extruded film due the slow production, and the extra energy costs of solvent recovery.

2.5 Matrix: Polycarbonate

Polycarbonates (PC) are high-molecular weight, amorphous engineering thermoplastics. They have exceptionally high impact strength over a wide temperature range. This polymer is characterized by a combination of toughness, heat and flame resistance,

transparency and dimensional stability. In addition, meets the FDA regulation for the use of the polymer in food-contact and medical applications.

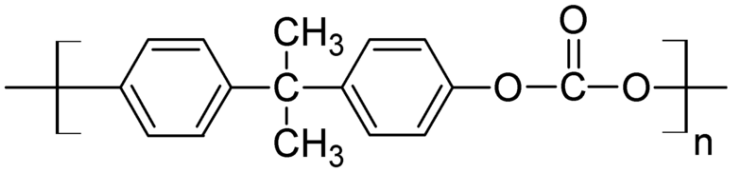


Figure 2.1. Chemical structure of repeating unit of Polycarbonate.

Polycarbonate is an insulator material with a resistivity of the order of 10^{11} Ω·cm. His melting point is at 265ºC and the glass transition is very high (150ºC).

All these properties make polycarbonate suitable for many applications such as power-tool housing, safety helmets, exit signs, microwave ware, solar cell covers, door and window hardware, automotive instrument panels, bottles, bus seats, interior aircraft parts, food packaging, coatings, etc. [17]

2.6 Filler: Silver Nanowires

Nanowires are nanostructures that have a thickness or diameter constrained to less than 200 nm and an unconstrained length. Different material nanowires exist, such as SiO_2, TiO_2, ZnO, Si, InP, GaN, MoS_2, WS_2, MoSI, Ni, Pt, Au, Ag, etc.

Silver nanostructures have been used as filler for nanocomposite and different properties have been obtained. Bactericidal properties have been obtained using silver nanoparticles[13]. Silver nanowires used as filler provides to the nanocomposite better thermal properties[7] and electrical properties[18].

Ag nanowires were synthesized in this project. Different synthetics strategies have been used in the bibliography to obtain silver nanowires. Wet syntheses are the most used and more or less all of them follow the same Ag nanowires formation steps[19]. With the first silver ions, different Ag nanoparticles were formed, decahedral multiple twinned particles (MTP) serve as seed for the Ag nanowires formation growing in one direction due to the existence of twin defects in the ends of the nanowires.

So far a large number of solvents and capper agents have been used to control the anisotropic growth of silver seeds and nanowires. Capper agent is very important for the silver nanowires synthesis because almost all methodologies are based on the absorption of this capper agent on certain faces to obtain the anisotropic growth. Different capper agents were used for the synthesis as PVP[2,3,20,21], CTAB[22], Sodium Dodecylsulfonate (SDS)[23], Vitamin B2[24], etc.

Polyol method is a typical method introduced by Fievet et al.[25], where polyvinylpyrrolidone (PVP) is used as a capper agent and a polyol is used as solvent, normally Ethylene Glycol. In this synthesis is very important the low concentration of silver in the initial steps in order to obtain high concentration of MTP that are more thermodynamically stable. Base on polyol method, Xia and co-workers also developed a salt-mediated polyol process to prepare Ag nanowires. In this synthesis, salt is added to

the reaction that causes an influence in the morphology of the final products. NaCl, $Fe(NO)_3$, $CuCl_2$ and CuCl are examples of chloride based salts that are used in this synthesis[4,26,27]. The addition of chloride ions causes enhanced oxidation called oxidative etching and preferential etching of polycrystalline nanoparticles, leaving only MTP to growth.

Seed-mediated growth approach is used to the formation of Ag nanowires, In this process, seeds of Ag or other metals as Au were prepared before the synthesis of the silver nanowires, and then the silver nanowires growth from this seeds[28,29]. Seedless and surfactantless wet chemical synthesis has been developed in order to obtain silver nanowires without impurities, where silver is reduced by sodium citrate in presence of NaOH[30].

Soft template method is another approach to get silver nanowire structure where mesophases structures are obtained from self-assembly from surfactant. This method depends on the restriction of micelles to guide the 1D growth of silver nanowires, instead the selective adsorption of the surfactant as in surfactant-assisted methodologies[31].

2.7 Electrical theory

Resistivity is property that can be measured for the electrical characterization of nanocomposite. For the calculus of the resistivity, complex impedance is measured using an impedance analyzer.

Electrical impedance is the measure of the opposition that a material presents to the passage of a current when an alternating current (AC) is applied. Impedance extends the concept of resistance from DC (Direct Current) to AC (Alternating Current)[32]. Impedance is the voltage/current ratio at a particular frequency. If we apply the ohm's law to a circuit with alternating current, where voltage and intensity are sine waves and the phase shift between intensity and voltage is the phase angle (ϕ). The following forms are used to represent the complex impedance:

$$R = \frac{V}{I} \quad \text{Ohm's law}$$

$$V = |V|\cos(\omega t) = |V|\, e^{j\omega t}$$

$$I = |I|\cos(\omega t - \phi) = |I|\, e^{j(\omega t - \phi)}$$

$$Z = \frac{V}{I} = \frac{|V|}{|I|}\frac{e^{j\omega t}}{e^{j(\omega t - \phi)}} = |Z|\, e^{j\phi}$$

Figure 2.2. Ohm's law extended to the alternating current obtaining complex impedance.

The magnitude of the complex impedance is the ratio of the voltage amplitude to the current amplitude. The phase of the complex impedance is the phase shift by which the current is ahead of the voltage. The complex impedance is represented usually using

complex numbers, Figure 2.3. shows the Cartesian and Polar form of the impedance where R is the resistance, X is the inductance and Z is the impedance. Impedance can be divided in the real part (resistance) and the imaginary part (inductance).

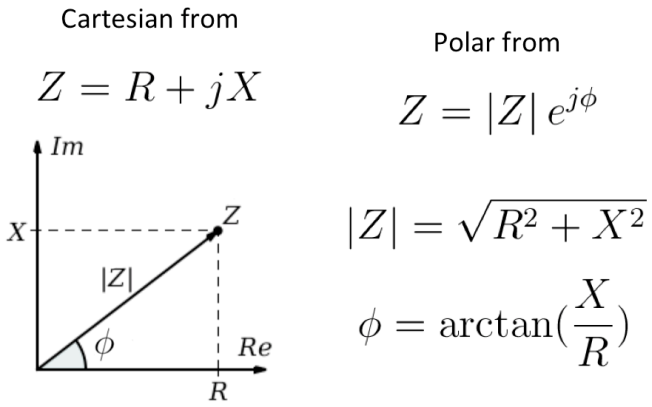


Figure 2.3. Phasor diagram and complex impedance in Cartesian and polar forms.

Phasor (phase vector) diagrams are used to represent the complex impedance. The usual reference for zero phase is taken to be the positive x-axis and is associated with the resistor since the voltage and current are in phase. The length of the phasor is proportional to the magnitude of the quantity represented, it is the voltage/intensity ratio; and the angle represents the difference in phase between voltage and intensity.

This phase shift occurs when the circuit is associated to a resistor with a capacitor or an inductor. A capacitor is a passive component, which stored energy in form of electrostatic field. An inductor is a passive component that stored energy in form of magnetic field. The voltage across a capacitor lags the current through it by a phase of π/2, while the voltage across and inductor leads the current through it by π/2. The following formulas represent the complex impedance of a resistor (A), inductor (B) and capacitor (C).

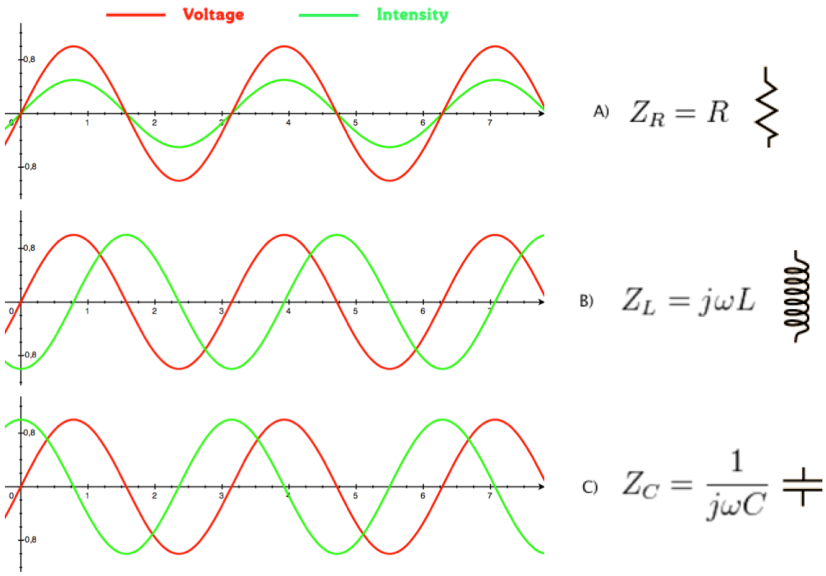


Figure 2.4. Behaviours of different electronic components with different impedance.

From this formula, when an inductor is connected to direct current (ω = 0), the component acts as a short circuit because the impedance is zero. In the case of a capacitor; when it is connected to direct current acts as an open circuit because the impedance is infinite.

These are the theoretical behaviours of the different components, but in the nature, the materials can be represent as a combination of resistances, inductances and capacitances, this behaviour is represented by the impedance, that measure the relation between the voltage that is applied to a material and the intensity that runs through the material.

Series association of resistor and capacitor/inductance result in the following phasor diagrams:

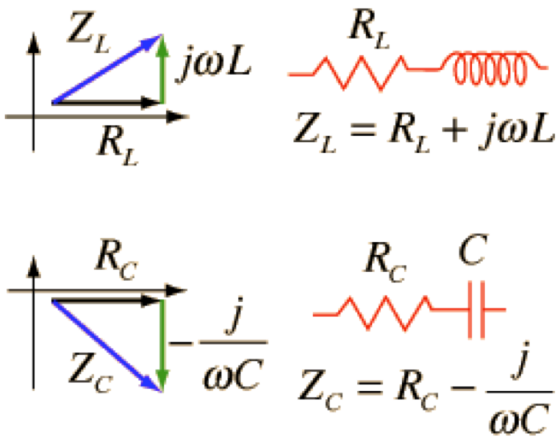


Figure 2.5. Resistance-Inductance and Resistance-Capacitance associations.

To sum up, complex impedance is a measure of the opposition of a material to the alternating current and shows the electrical conductivity behaviour of a material; and phasor diagrams are used to show the impedance of a material.

3 EXPERIMENTAL SECTION

3.1 Silver Nanowires synthesis

Synthesis of silver nanowires was carried out by two different methodologies, conventional synthesis and solvothermal one. These two syntheses are based on the polyol method that consists in the use of a polyol as solvent. With polyol method different silver structures can be obtained as shows in Figure 3.1.

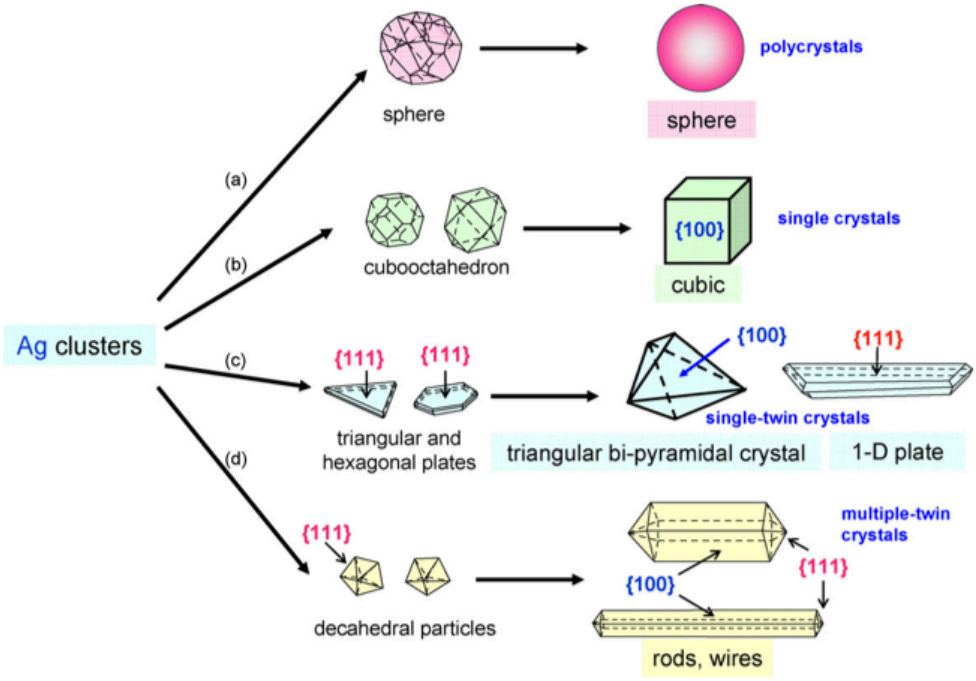


Figure 3.1. Different silver nanostructures obtained using polyol method[33].

Silver nitrate ($AgNO_3$) is used as metal precursor and ethylene glycol as solvent. When temperature increases, Ethylene glycol acts as a reducing agent and metallic silver structures are formed. The addition of polyvinylpyrrolidone (PVP) is used to stabilize and protect the nanostructures from sintering. Firstly twinned decahedra silver nanoparticles must be formed in order to obtain silver nanowires. Decahedra particles are the naturally abundant seed morphology. The silver ions are preferably linked to the twin defects of these particles, leading to a initial 1D growth. The PVP in the solution is adsorbed reversibly by the surface of the initial nanoparticles, providing a dynamic capping layer that stabilizes the particles in the solution and leads their growth through preferential direction due the PVP is bonded to some specific facets[2]. For instance, PVP is absorbed preferentially in {001} side facets than the {111} faces that are in the ends of the nanowires. This leads in growth of long silver nanowires as shown in Figure 3.2.

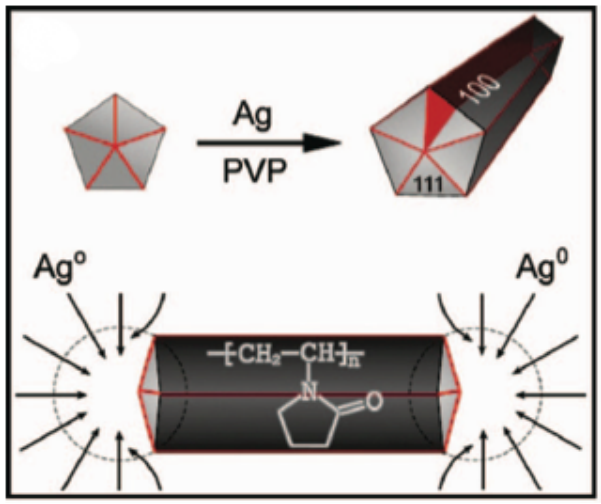


Figure 3.2. Silver Nanowire formation mechanism, where PVP is adsorbed in (100) crystal faces [34].

3.1.1 Materials and equipment

Silver Nitrate 99,8% (Panreac), Polyvinylpyrrolidone Mw-55.000 (Aldrich), Sodium Chloride (Aldrich), Ethylene glycol anhydrous 99,8% (Sigma-Aldrich) were used as reactives for the wires synthesis without a further purification.

The following table shows the equipment used in the project:

Equipment	Brand	Model
Syringe pump	kdScientific	Kds-100-ce
Heating plate	IKA	RCT basic
Centrifuge	Jouan	B 4i
Oven	Memmert	

The autoclave for the solvothermal synthesis consists of a stainless steel frame and a removable Teflon inner body. Designed by the working group and manufactured by Precision Mechanics Polytechnic Service of the University of Zaragoza.

The stainless steel structure consists of a base disk, a steel body, a rupture disc, two sealing pieces separated by a spring and a screw cap. Inside lies the body of 43 cm^3 Teflon capacity consisting of a cylinder and a cap.

3.1.2 Conventional synthesis

Silver nanowires were synthesized using polyol process based in Y. Sun [35]. In a typical synthesis 14 ml of EG was preheated in a 100-ml flask at 180 ºC during one hour. Then an EG solution of $AgNO_3$ (0,085M) and EG solution of PVP (0,13M) were simultaneously added into the initial ethylene glycol at a rate of 0,375 ml/min during 16 minutes using two syringe pumps. The reaction mixture was heated at 180 ºC for 40 minutes. Magnetic stirring was maintained through the synthesis.

The molar ratio between PVP and silver nitrate was changed in order to optimize the product obtained. The following table show the experiments with the molar relations that have been performed:

Table 2.1. Molar concentration of the different experiments.

$AgNO_3$	PVP
0,085M	0,13M
0,06M	0,13M
0,04M	0,13M

$AgNO_3$	PVP
0,085M	0,15M
0,085M	0,1M
0,085M	0,085M

3.1.3 Solvothermal synthesis

The same polyol method is used in this synthesis in order to obtain silver nanowires; the methodology of this synthesis was based on a solvothermal method reported by D. Chen publication [20].

In a typical synthesis procedure, 10 ml ethylene glycol solution of 0,15M PVP is prepared and injected drop by drop using a syringe into 10 ml of magnetically stirred EG solution of 0,1M $AgNO_3$. The solution is magnetically stirred during 5 minutes and then it was put into a 45 ml Teflon-lined autoclave. It is sealed and maintained at 160ºC for 2.5 hours in the oven. Afterward, natural cooling to room temperature is performed in order to avoid agglomeration.

In order to wash the suspension, 60 ml of acetone is added and then the suspension was centrifuged at 3000 rpm for 10 minutes, supernatant is eliminated and silver nanowires were dispersed in acetone. This process is repeated three times in order to eliminate all the reactive. Finally, silver nanowires were dispersed in ethanol in order to characterise them.

Different parameters of the synthesis were changed in order to obtain different sizes of silver nanowires:

- Sodium Chloride (0,1 mM) was added to the PVP solution in order to test if chloride ions increase the nanowires/nanoparticles yield of the synthesis [3,33,36].
- $AgNO_3$ concentration was fixed and PVP concentration was changed using the following concentrations: 0,1M; 0,13M; 0,15M; 0,17M and 0,2M.
- Sample was dried at 60ºC in ethanol.
- Sample was washed with and without the addition of acetone as explained above.
- Sample in ethanol was exposed to the solar light during one day.

3.2 Preparation of nanocomposites

Nano-composites of polycarbonate with different loadings of silver nanowires were prepared and characterized.

3.2.1 Materials and equipment

Poly (Bisphenol A carbonate) (Aldrich), tetrahydrofuran 99% (Sigma-Aldrich), dichloromethane stabilized with 150 ppm of amylene 99,8% (Aldrich), chloroform stabilized with 150 ppm of amylene 99,8% (Scharlau) and absolute ethanol were used for the preparation of nanocomposites.

Silver nanowires obtained using solvothermal method (0,1M $AgNO_3$ / 0,15M PVP / 0,1mM NaCl) were used.

The following table shows the equipment used in the project:

Equipment	Brand	Model
Ultrasonic bath	Sonitech	UD100SH-3L
Heating plate	IKA	RCT basic
Oven	Memmert	

Petri dish are made of Teflon with the following dimensions: External diameter (90mm), internal diameter (80mm) and height (15mm) manufactured by Precision Mechanic Polytechnic Service of the University of Zaragoza.

3.2.2 Solubility test

In order to obtain uniform polymeric films, a deep study was carried out to determine the optimal process conditions.

Different solvents (Toluene, tetrahydrofuran, Dichloromethane and chloroform) were tested to dissolve the polycarbonate and the silver nanowires.

3.2.3 Casting evaporation method

In a typical procedure, 1g of polycarbonate is dissolved in 30 ml of organic solvent (THF/Chloroform/Dichloromethane) using ultrasonic bath during 15 minutes. The Ag nanowires in the proportion necessary (1% w.t.) were dispersed in 30 ml of the same organic solvent using ultrasonic bath during 30 minutes. The dispersion of Ag nanowires is added drop by drop to the solution of polycarbonate under magnetic stirring. The mixture is immersed in an ultrasonic bath for 30 minutes. The suspension is deposited in a petri dish and allowed to evaporate until the solvent is removed. Figure 3.3 shows a scheme of the casting evaporation method.

Different ways of evaporation were performed:

- Evaporation at room temperature.
- Evaporation in oven at 60ºC and 65ºC.
- Evaporation in an ultrasonic bath.

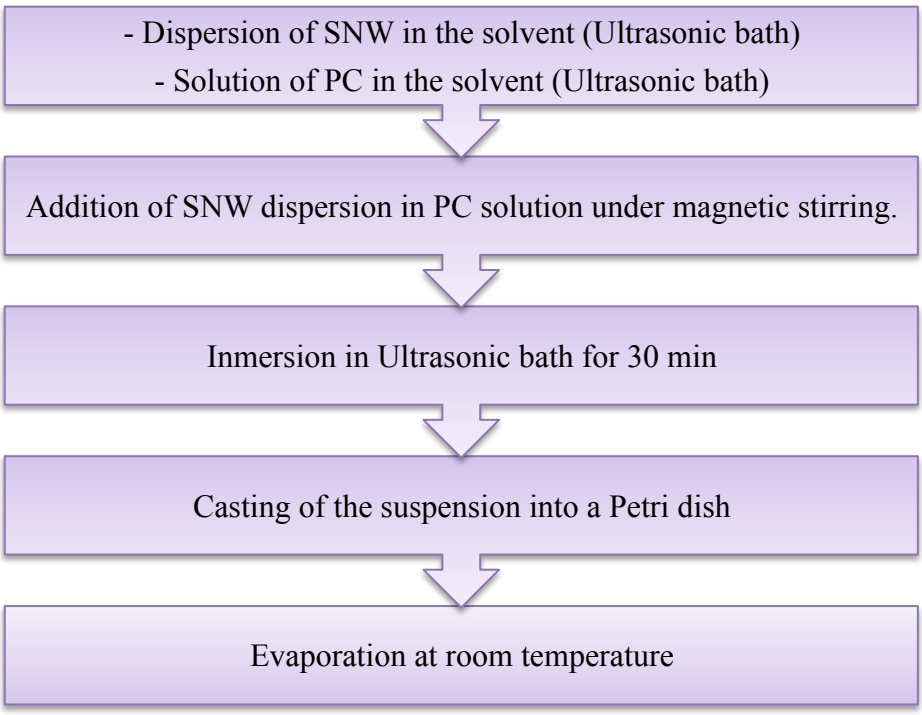


Figure 3.3. Casting evaporation method steps.

3.2.4 Casting / pull rod method

The procedure is the same as for the casting evaporation method but after adding the dispersion of AgNW, the mixture is heated at 70ºC under magnetic stirring in order to evaporate almost all the THF. When the suspension is reduced to 10 ml, it is spread in a glass plate and drag with a rod (Figure 3.4). The solvent is finally evaporated in a few minutes. Vacuum treatment (50mbar / 80ºC / 24 hours) is applied to the nanocomposite film in order to eliminate all the residual solvent. Figure 3.5 shows a scheme of the casting / pull rod method.

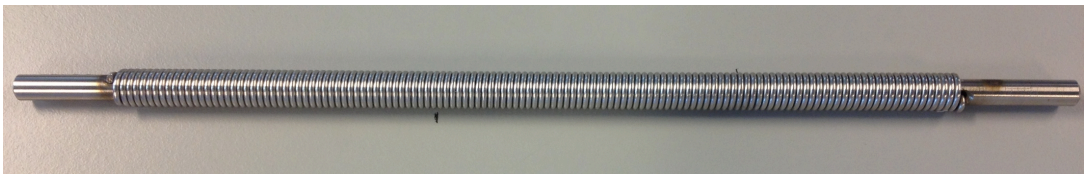


Figure 3.4. Rod used for the development of polymeric films.

Two different procedures have been carried out in order to disperse the silver nanowires in the solvent:

- **Dry:** Silver nanowires in ethanol were dried and then redispersed in THF.
- **Dispersion:** Silver nanowires in ethanol was centrifuged, then the ethanol is eliminated and the precipitated is redispersed in THF.

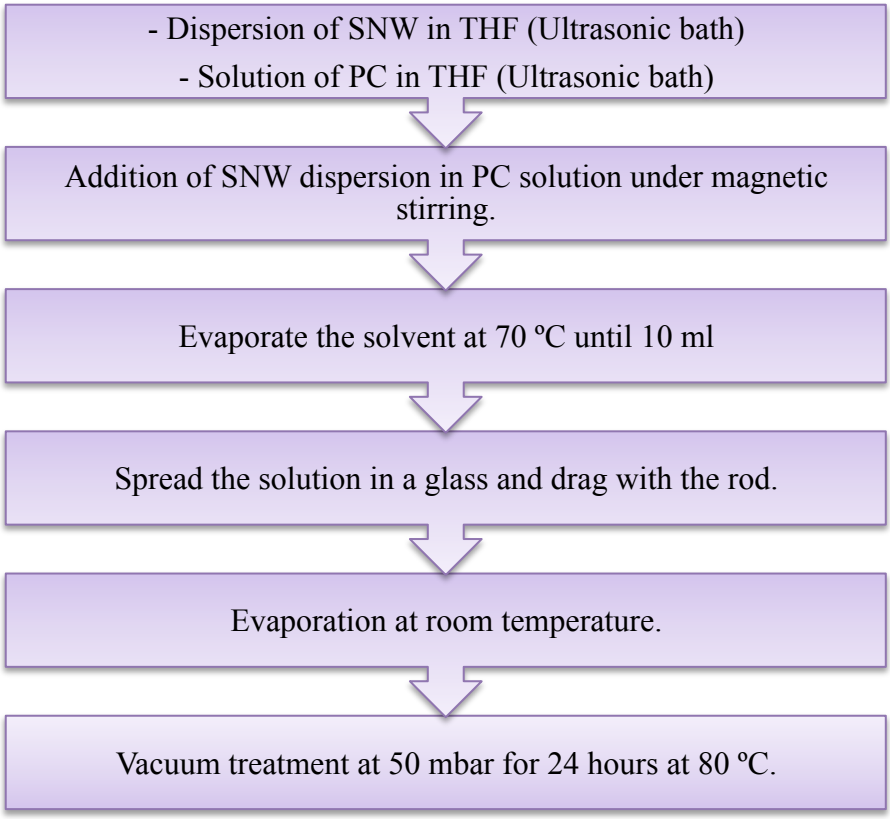


Figure 3.5. Casting / rod wire method steps.

Nanocomposite films with different silver nanowires concentration were prepared using this method. In the case of Dry method 0,5wt%, 2wt% and 3wt% ones were prepared. For Dispersion method, the following concentrations were prepared: 0,02wt%, 0,04wt%, 0,08wt%, 0,15wt%, 0,25wt%, 0,75wt%, 1xt%, 1,5wt%, 3wt% and 4,5wt%.

3.3 Characterization

3.3.1 Characterization of Silver Nanowires

Characterization of SNW was very important in order to optimize the synthesis and later to obtain additional information about them.

Scanning Electron Microscopy (SEM) is a technique that images a sample by scanning it with a high-energy beam of electron. Secondary electrons were used in this equipment to obtain information about the surface topography, the size and the morphology of the nanowires. FEI Inspect F (Institute of Nanoscience of Aragon) equipment was used to obtain the images for this project. Ag nanowires samples were prepared depositing a drop of the sample (SNW dispersed in ethanol) in a carbon conductive tape.

Transmission Electron Microscopy (TEM) is a microscopy technique where a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. The image is formed from the interaction of the electrons transmitted through the specimen. FEI Tecnai F30 Microscope was used to obtain

information about the morphology of cross-section of SNW. Silver Nanowires were embedded in an epoxy resin and cut with a diamond blade in a microtome.

Selected Area Electron Diffraction (SAED) is a crystallographic technique that can be performed inside a TEM microscope. In this technique, electrons are treated as wave like, the atoms of the sample act as a diffraction grating to the electrons, which are diffracted. The result is an image with series of spots, each point corresponds to a satisfied diffraction condition of the sample's crystal structure; namely, points appear when Bragg's law is fulfilled. This technique is used to obtain information about the crystallographic structure. These experiments were carried out using the same equipment as TEM analysis. The samples were prepared depositing a drop of the sample (SNW dispersed in ethanol) in a TEM grid.

X-ray powder diffraction (XRD) is a technique that uses X-ray in order to obtain information about the crystalline phases that are in the sample. It consists in a collimated X-ray beam that is scattered by the crystalline phases of the sample in different angles. This scattered radiation is collected on a flat plate detector where appear rings around the beam axis. Each ring corresponds a diffraction peaks and are represented in a spectrum of the intensity of scattered radiation as function of the scattered angle. D-Max Rigaku /2500 X-ray diffractometer with a cooper anode and graphite monochromator to select CuKα radiation, with $\lambda = 1.5418$ Å, between the angles interval from 30º to 90º with a speed 0,03º/s.

UV-Vis spectroscopy (UV-Vis) is an absorption spectroscopy that works in the ultraviolet and visible spectral region. The equipment measures the intensity of the light reflected from a sample and compares it to the intensity of light reflected from a reference material. JASCO V670 equipment was used to analyze the silver nanowires. Ag nanowires dispersed in water were analyzed using this technique.

3.3.2 Characterization of Nano-composites

Thermo-gravimetric analysis is a technique that measures the weight changes with the temperature. In this project, Mettler Toledo TGA/SDTA 851 equipment has been used with the following conditions: from room temperature to 850 ºC with a heating rate of 10ºC/min with an air flux of 30 ml /min. This technique is used to determine the load of filler inside nano-composites, in addition, gives information about the polymer degradation temperature.

Scanning Electron Microscopy (SEM) with a backscattered detector has been used. Backscattered electrons were used in this equipment to obtain information about the distribution of the nanowires in the polymer. Backscattered electrons consist of high-energy electrons from the beam that are reflected or backscattered out of the specimen interaction volume by elastic interactions. These electrons are more sensitive to heavy elements (high atomic number), so this technique is used to obtain high contrast between different elements. The interaction volume of this technique is about 10 nm, so the images correspond to surface composition. Nano-composites were prepared in a holder and then covered with a gold layer in order to make the sample conductive.

Optical microscopy is a technique that uses visible light and a system of lenses to magnify images of small samples. Olympus BX-41 is used in order to obtain images where silver nanowires can be observed inside the nano-composite. This technique provides information about the distribution and uniformity of fillers inside the films.

3.4 Conductivity assays

The nano-composites were tested measuring their resistivity using an impedance-meter. Figure 3.6a shows a scheme of the assembly to perform the measure.

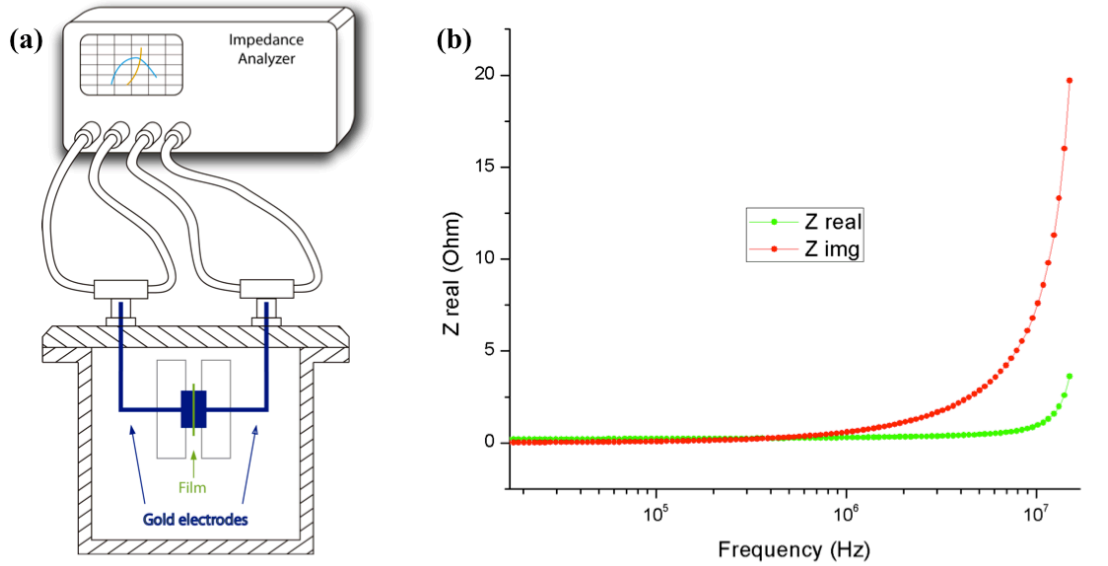


Figure 3.6. Scheme of the assembly (a) and the result of a conductivity measurement (b).

In order to carry out the experiment, conductivity module was used to place the sample and create contact between the sample and the electrodes. This conductivity module has two gold electrodes with 0,618 cm^2 superficial contact area. The sample is placed between the two electrodes and then all is constrained using 4 screws. Transversal resistivity across the film is measured in this experiment. The experiment is performed at room temperature inside a closed cell.

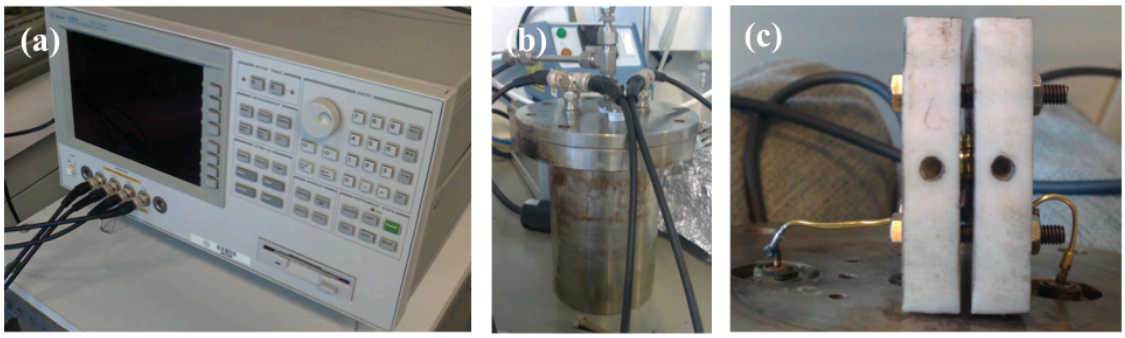


Figure 3.7. Equipment used for the conductivity measurement: (a) Impedance Analyzer, (b) Cell and (c) Conductivity module with gold electrodes.

Agilent 4294A Precision Impedance Analyzer was used to measure the complex impedance of the film. The equipment applies a frequency to the electrodes and measures the real and imaginary part of the impedance. This equipment provides information about the impedance as function of the frequency. The equipment does a frequency sweep between 40 Hz and 15 MHz. Figure 3.6b. Shows the information that obtained from the conductivity measurement.

To obtain the conductivity of each sample, imaginary impedance is plotted as function of the real impedance (Nyquist plot) [37]. When the imaginary impedance is zero, the phase angle is zero and all the contribution corresponds to the real impedance. The real impedance corresponds only to the relation between the intensity and the voltage, so when the imaginary impedance is zero, the real impedance is the resistance.

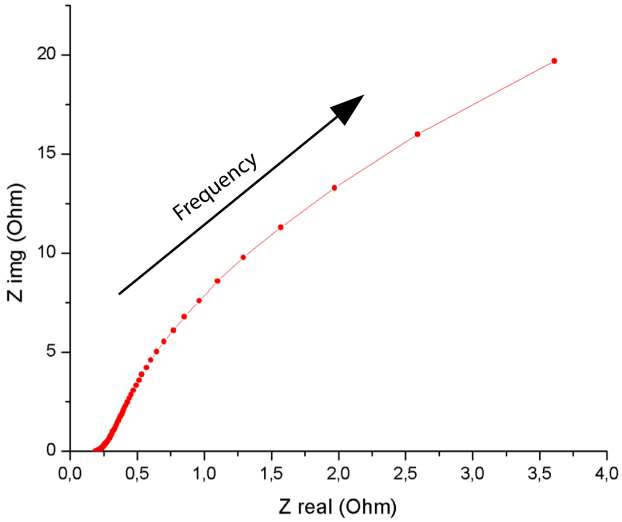


Figure 3.8. Representation of a Nyquist plot.

Resistivity of the material (σ) can be obtained from the resistance (ρ), the thickness of the sample (L) and the area of contact (A). As the conductivity is the inverse of the resistivity, the following formula is used to calculate the conductivity of the films. The area of contact is fixed by the electrodes, is 0,618 cm^2. Every sample has been analyzed at three different points of the film.

$$\sigma = \frac{1}{\rho} = \frac{L}{A \cdot R}$$

4 RESULTS AND DISCUSSION

4.1 Conventional synthesis

The nanowires were characterized using Scanning Electron Microscopy. The micrographs show the formation of silver nanowires and the nanowires/nanoparticles ratio.

In order to obtain higher Ag nanowires/Ag nanoparticles ratio, the concentration of the solutions of the metal precursor ($AgNO_3$) and the capper agent (PVP) has been changed[38]. For this, different PVP and $AgNO_3$ concentrations have been used as has been explained in the experimental procedure section. First, the $AgNO_3$ concentration (0,085M/0,06M/0,04M) was varied keeping the PVP concentration (0,13M) was fixed. It has also been modified the PVP concentration (0,085M/0,1M/0,13M/0,15M) keeping the $AgNO_3$ concentration fixed at 0,085M.

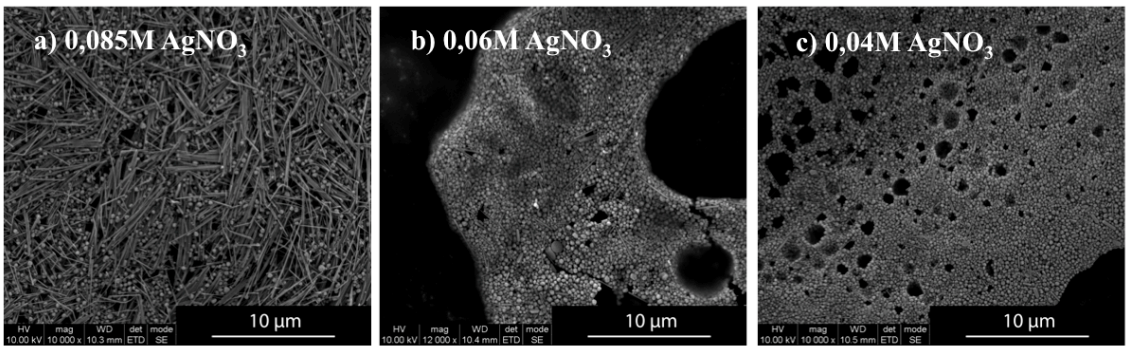


Figure 4.1. Results of the synthesis with PVP concentration fixed at 0,13M and different $AgNO_3$ concentrations.

When the PVP concentration (0,13M) was fixed, with 0,085M Silver nitrate a mixture of nanowires and nanoparticles were obtained; but when the concentration of silver nitrate was decreased to 0,06M, only a few nanowires were obtained, mostly all the suspension is composed by nanoparticles. In the case of 0,04M, only nanoparticles were obtained (Figure 4.1).

At a PVP concentration of 0,13M low yield of nanowires were obtained, so the concentration of the silver nitrate was fixed at 0,085M and the concentration of PVP was changed (0,085M / 0,1M / 0,13M / 0,15M).

As Figure 4.2 shows, with 0,1M practically all the dispersion obtained consisted of nanoparticles. In foreclose, for the synthesis with 0,15M of PVP a mixture of silver nanowires and particles was obtained. And finally, when the PVP and the silver nitrate concentration was 0,085M, high quantity of silver nanowires were obtained. Only a few small nanoparticles appear in the dispersion. These concentrations were chosen as the best conditions to obtain silver nanowires with this methodology.

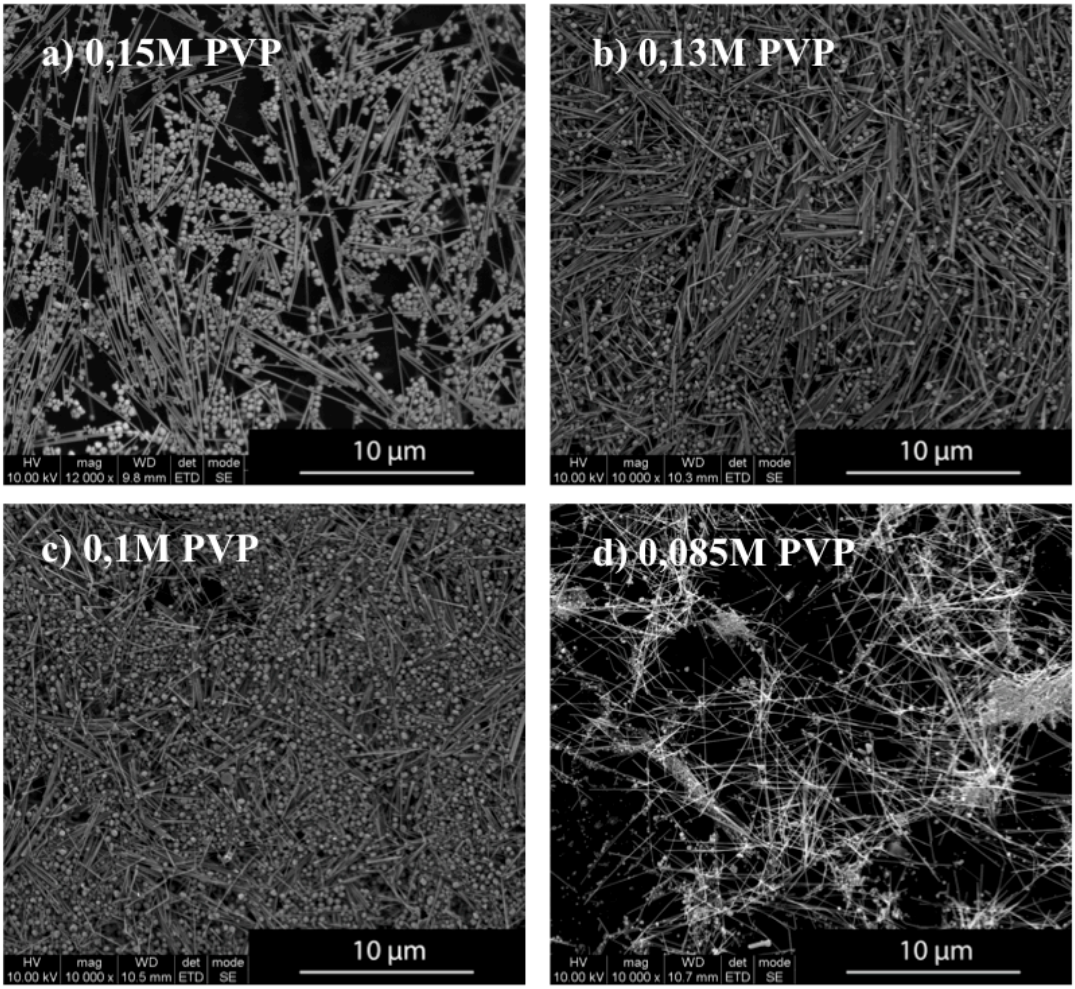


Figure 4.2. Results of the synthesis with $AgNO_3$ concentration fixed at 0,085M and different PVP concentration.

Several syntheses were carried out using this methodology in order to test the reproducibility. In some cases silver nanowires with a high yield were obtained, however, in other cases only nanoparticles were obtained. Following images show different synthesis using the same parameters (Figure 4.3).

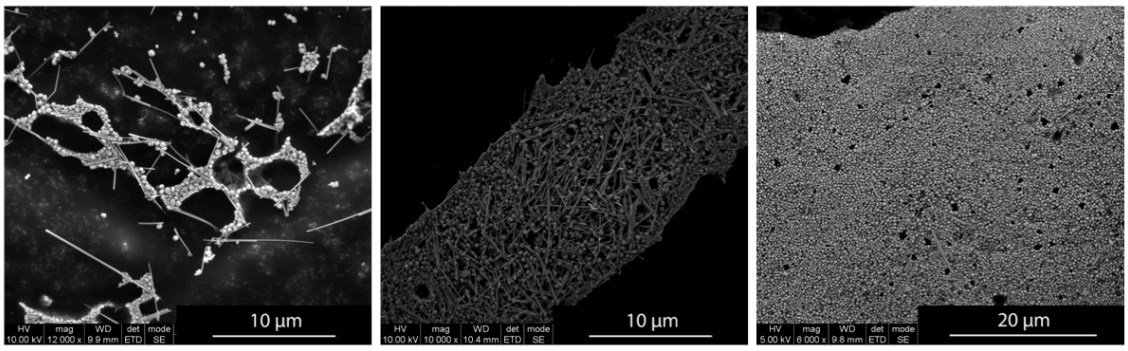


Figure 4.3. Three different synthesis (0,085M PVP / 0,085M $AgNO_3$)

It can be concluded that the synthesis is not reproducible. This low reproducibility can be attributed to different causes:

- Oscillation of the oil bath temperature.
- Temperature gradient between the PVP/$AgNO_3$ solutions and the preheated EG.
- In some cases, Ag seeds were formed in the solution before it is added.

Because of these problems, other methodology was chosen in order to obtain a better yield of silver nanowires.

4.2 Solvothermal synthesis

A new methodology was used to synthesize the Ag nanowires as explained in the experimental section. The products of this synthesis were characterized by SEM and TEM microscopies, XRD and UV-Vis spectroscopy.

4.2.1 Scanning Electron Microscopy (SEM)

SEM images provide information about the morphology and the size of the nanowires. In this section SEM images of the different experiments will be shown, analysing different parameters of the process:

- The addition of sodium chloride.
- The variation of molar ratio (PVP/$AgNO_3$) varying the PVP concentration (1M/1,3M/1,5M/1,7M/2M) keeping the $AgNO_3$ concentration (0,1M) constant.
- Influence of the after treatment (Drying and acetone wash).

Addition of sodium chloride

As seen in Figure 4.4, high yield of nanowires/nanoparticles were obtained using this method. The influence of the addition of NaCl in the synthesis was studied because Tsuji, M. [33]reported that chloride ions contribute to obtain more nanowires than nanoparticles. The $AgNO_3$ concentration (0,1M) and PVP concentration (0,15M) was fixed. Figure 4.4a and c shows images at different magnifications of the same synthesis without the addition of NaCl. As can be seen in these images, large amount of polycrystalline nanoparticles appear in the product of the synthesis. In the Figure 4.4b and d that correspond to different magnifications of the same synthesis, NaCl was added to the synthesis. This better selectivity is due the chloride ions; spherical particles are dissolved due to oxidative etching of Cl^- ions. Spherical nanoparticles are more active than single and twinned nanoparticles because they have more defects and chloride ions attack and dissolve them preferentially. Single crystals as nanocubes and twinned crystals as decahedral nanoparticles and their growth into Ag nanowire are favoured by the addition of NaCl.

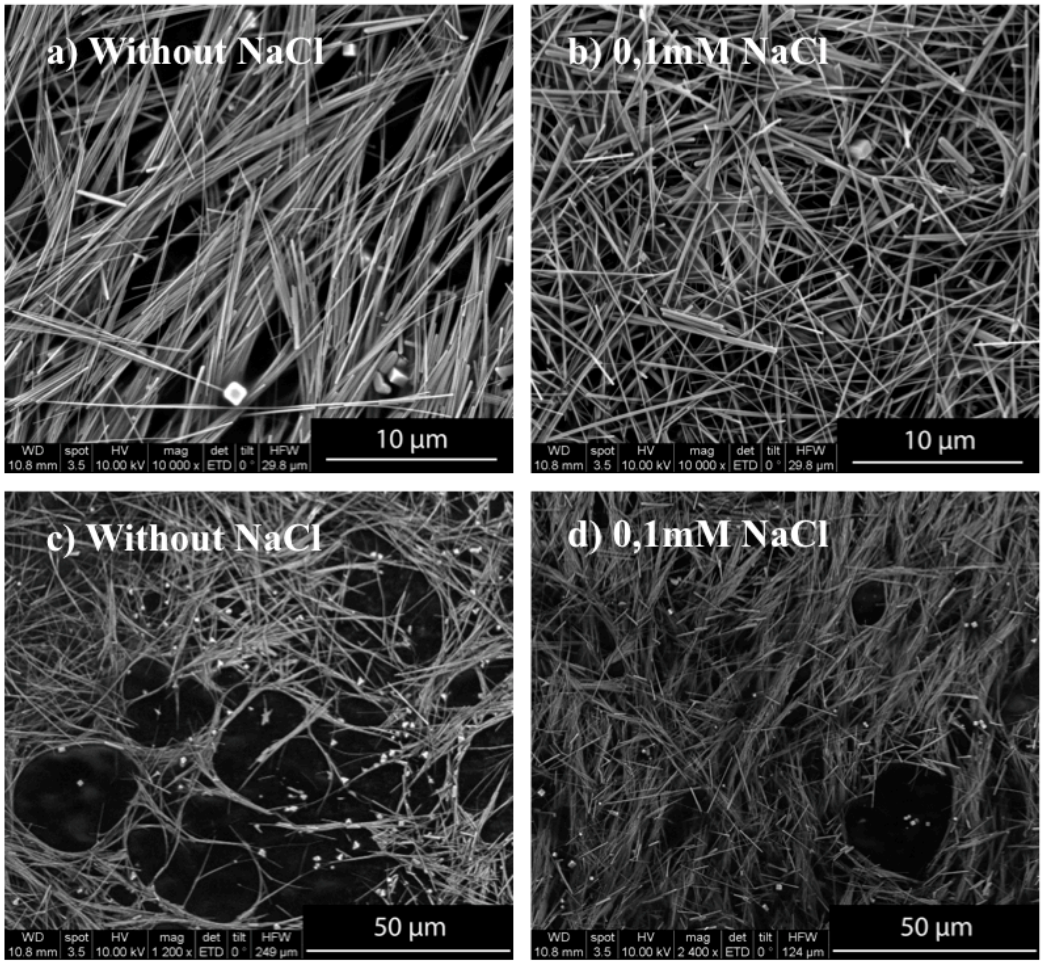


Figure 4.4. SEM images of Silver Nanowires using solvothermal method. (a) and (c) With NaCl (0,1 mM); (b) and (d) without NaCl.

In addition, chloride ions provides electrostatic stabilization for the initially formed Ag seeds, and chloride ions form AgCl nanocrystallites and reduce the concentration of free silver ions in the solution, this behaviour leads a slow release process of silver which guide the high-yield formation of the thermodynamically more stable MTPs (Multiply Twinned Particles) require for the silver nanowires. It can be concluded that with the addition of NaCl, the quantity of undesirable nanoparticles decreases in comparison with the synthesis without the addition of NaCl.

Variation of molar ratio

In order to obtain Ag nanowires with different aspect ratio, the molar ratio between the repeating unit of PVP and $AgNO_3$ has been modified[38]. Molar ratio has been changed varying the molar concentration of the capper agent (PVP) and keeping constant the molar concentration of metal precursor ($AgNO_3$) at 0.1M. Syntheses have been made at different concentrations of PVP: 0.1M, 0.13M, 0.15M, 0.17M and 0.2M. This synthesis has been carried out using NaCl (0,1mM). The results of this synthesis have been analysed using SEM and the images can be observed in Figure 4.5.

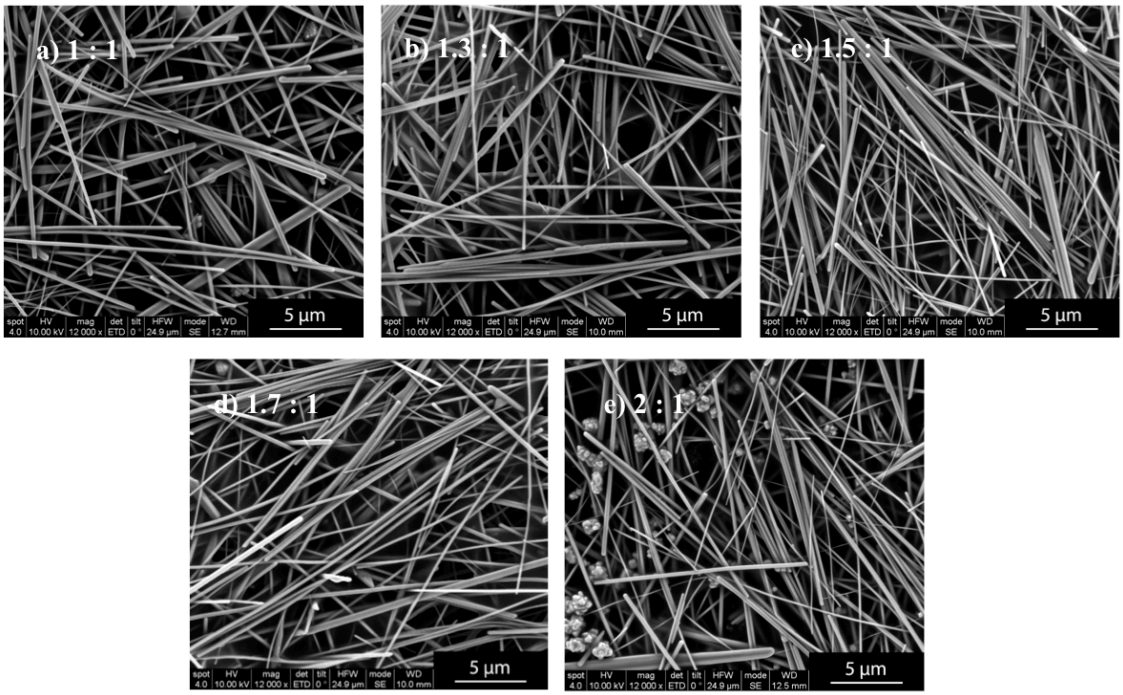


Figure 4.5. Aspect ratio of silver nanowires with different molar ratio between PVP and $AgNO_3$

From these images, the size distributions were calculated. The length is almost the same for all the synthesis independently of the molar ratio. This length was between 3 µm and 45 µm and the average was 10 µm. Figure 4.6 shows the distribution of the length of a synthesis (0,1M $AgNO_3$ / 0,15M PVP / 0,1mM NaCl). This distribution was obtained measuring around 500 nanowires.

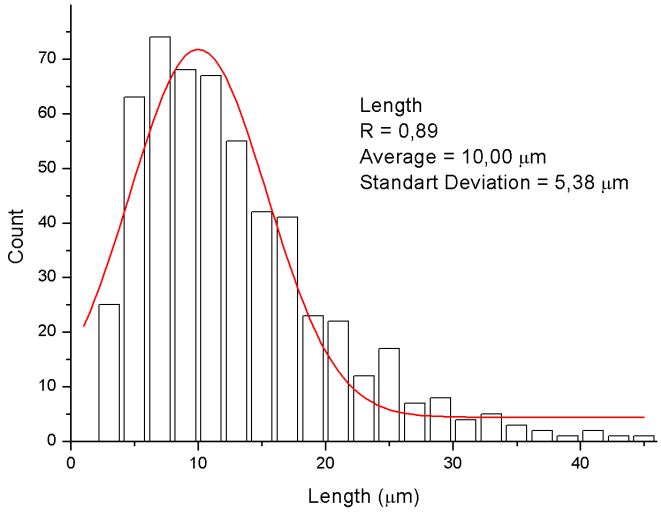


Figure 4.6. Distribution of length.

However, the mean diameter has a relation with the molar ratio used for the synthesis. Figure 4.7 shows the comparison between the fitted curves of the distributions of the different synthesis. To obtain the distribution, around 200 nanowires have been

measured in every sample. Even thought the standard deviation is too high, indicating that wide distribution of diameters is obtained in the synthesis.

With a PVP/AgNO3 ratio of 1.5: 1 Ag nanowires with 116 nm mean diameter were obtained, when the concentration of PVP is decreased to 1.3: 1, the mean diameter increases slightly to 129 nm. If we continue decreasing the PVP concentration to 1 : 1, the mean diameter continues increasing until 146 nm. Low PVP concentration would allow the growth of the seeds leading to wires with higher mean diameter.

When the molar ratio increases from 1.5 : 1 to 1.7 : 1, the mean diameter increases from 116 to 132 nm. If the molar ratio continues increasing until 2 : 1, the nanowires diameters continue increasing, the size dispersion is higher and some polycrystalline particles start to appear. With this molar ratio, the mean diameter is around 200 nm. This effect could be due the increase in viscosity of the solution than hinder the silver ions diffusion resulting in bigger seeds that produce nanowires higher diameter. Figure 4.7 shows a summary of the average of diameters that have been synthesized.

Molar ratio ($PVP/AgNO_3$)	Average (nm)	Standard Deviation
1 : 1	146,01	93,71
1.3 : 1	129,04	108,15
1.5 : 1	116,67	101,50
1.7 : 1	132,52	125,17
2 : 1	202,86	177,87

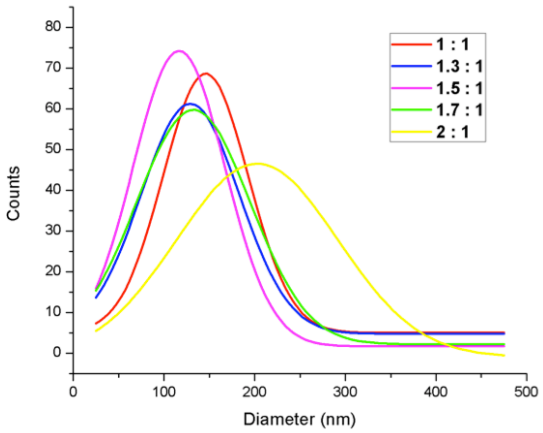


Figure 4.7. Aspect ratio comparison for the different synthesis.

These results indicate that the mean diameter size of silver nanowires can be controlled by the relative concentration of the precursors. This fact demonstrates the highly dependence of the molar ratio of PVP and $AgNO_3$ in the growth of silver nanowires. The length distribution is always the same distribution but the mean diameter can be tailored between 100 and 200 nm.

Influence of the after treatment

The influence of different post-treatments was analyzed. Figure 4.8 shows images of the same synthesis (0,1M $AgNO_3$ / 0,15M PVP / 0,1mM NaCl) that has been subjected to various treatments. Figure 4.8a shows the result of washing the synthesis without acetone and Figure 4.8b shows the result of washing with acetone as is described in the experimental procedure. If the two cases are compared, some nanoparticle appears in the sample without acetone and the sample appears to have some residual Ethylene Glycol due the problems to take images in the microscope. On the other hand, perfect silver nanowires appear in the sample with acetone. It can be concluded that the washing using acetone eliminate completely the residual solvent and also some silver nanoparticles can be eliminated.

In order to store the silver nanowires, they were dried as is explained in the experimental procedure. Figure 4.8c and d show SEM images at different magnifications of the same sample that has been dried. In the images, aggregation of the silver nanowires can be observed. In addition, the silver nanowires were twisted and deformed losing the morphology and the properties of the initial silver nanowires that were obtained from the synthesis.

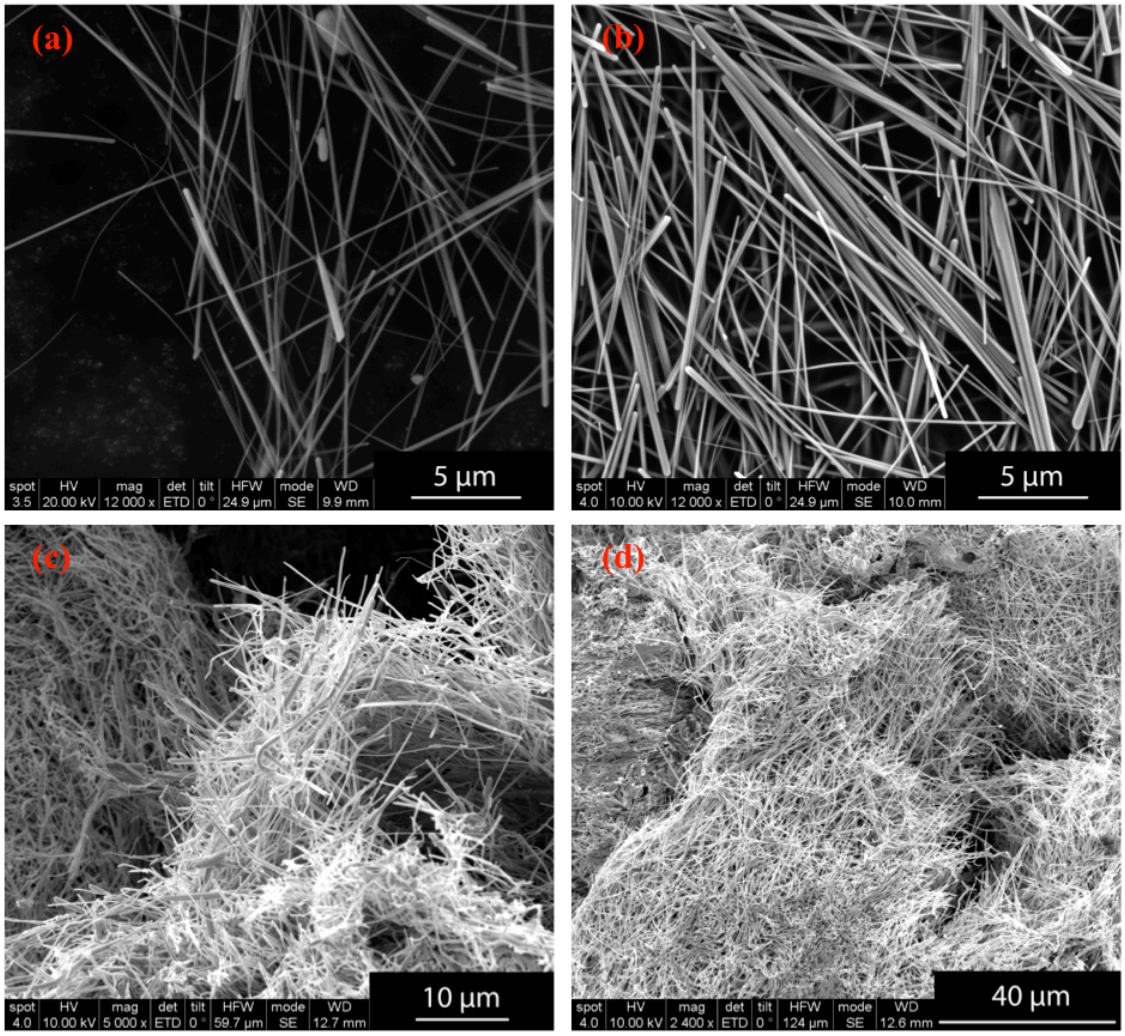


Figure 4.8. SEM images of samples with different treatments: without acetone (a), with acetone (b) and drying (c and d).

These results indicate that the better form of washing the silver nanowires is using acetone, and the better way to preserve the morphology and the properties of the silver nanowires is store the dispersion of the silver nanowires without drying.

4.2.2 X-ray diffraction (XRD)

X-ray diffraction confirms that the silver nanowires have a face centered cubic (FCC) structure that corresponds to crystalline silver. The peaks indexed can be observed in Figure 4.9. In this figure, the two different syntheses of conventional (one only with nanoparticles and another with a mixture of nanoparticles and nanowires) and the solvothermal synthesis are compared.

The peaks can be indexed as (111), (200), (220), (311) and (222) diffraction peaks that corresponds to a Face Centered Cubic structure (FCC) of silver. No differences can be observed between the synthesis methodologies. So, this technique is not appropriate to distinguish between nanoparticles and nanowires since both of them present the crystalline structure of silver. The lattice constant calculated from this pattern is 4,092 Å, which is consistent with the standard value of 4.086 Å[39].

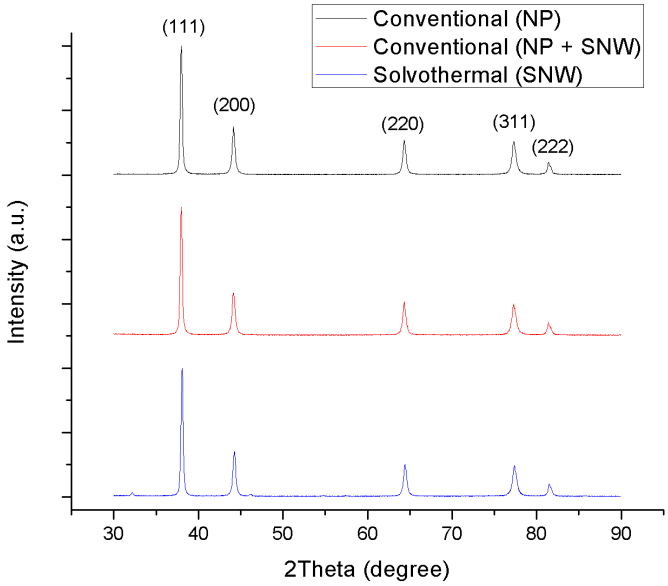


Figure 4.9. XRD spectra of the different synthesis.

4.2.3 UV-Vis spectroscopy

Silver nanowires have optical properties directly related to the surface plasmon resonances (SPR). UV-Vis absorption spectra of the Ag nanowires show two absorption peaks at 350 and 393 nm, which are attributed to the plasmon response of the transverse plasmon mode of long silver nanowires[1].

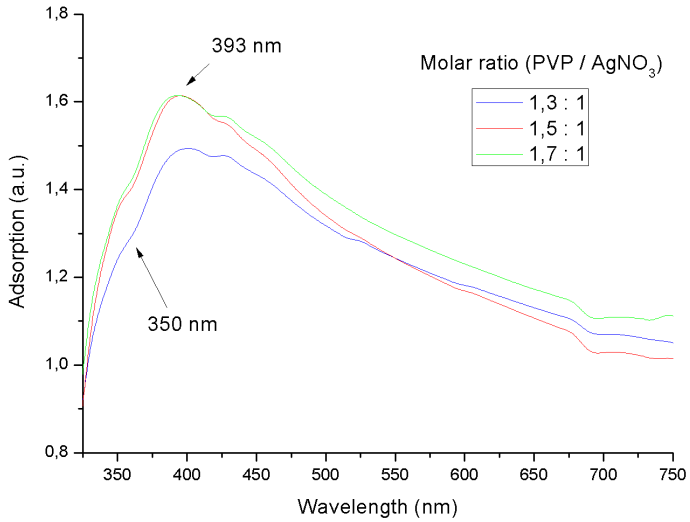


Figure 4.10. UV-Vis spectra of silver nanowires in water.

In our case, the UV-Vis spectra obtained from the different synthesis (molar ratio: 1:1/1,3:1/1,5:1/1,7:1/2:1) are similar. Figure 4.10 shows the spectra of samples with the following synthesis parameters: 0,1M $AgNO_3$, 0,13M/0,15M/0,17M PVP and 0,1mM NaCl. The spectra show two peaks at 350 nm and 393 nm, which should be attributed to the out-plane quadrupole resonance and out-of-plane dipole resonance of the Ag nanowires, respectively[2]. The peak that corresponds to the SPR of Ag nanoparticles (445 nm) is very small and insignificant in comparison with the peaks that correspond to the transverse plasmon of silver nanowires (350 and 393 nm). This means that our sample is mainly composed by silver nanowires.

4.2.4 Transmission electron Microscopy (TEM)

Transmission electron microscopy was used in order to obtain more information about the morphology of the prepared silver nanowires. The effect of the light in the suspension of silver nanowires (0,1M $AgNO_3$ / 0,15M PVP / 0,1mM NaCl) has to be analyzed. In addition, High Resolution TEM provides information about the crystallinity and morphology structure of this sample.

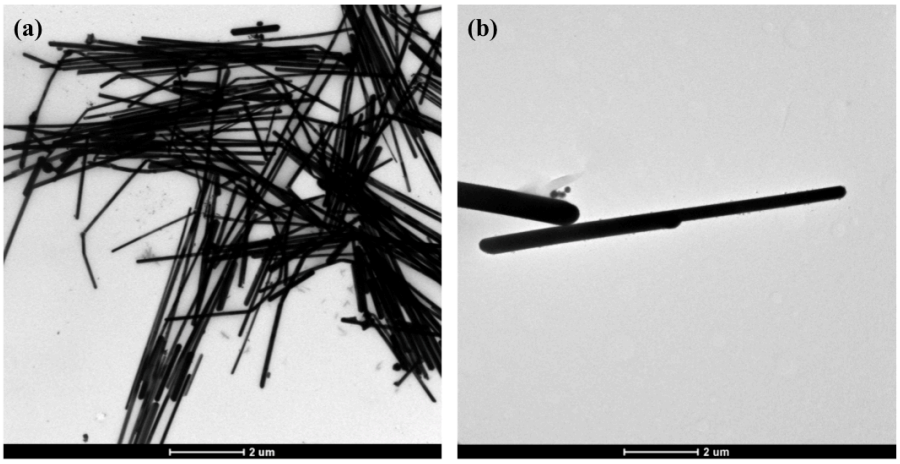


Figure 4.11. TEM images of silver nanowires.

Figure 4.11 shows images of the silver nanowires without the exposure to the solar light. This silver nanowires preserve the morphology and the size of the silver nanowires synthesized.

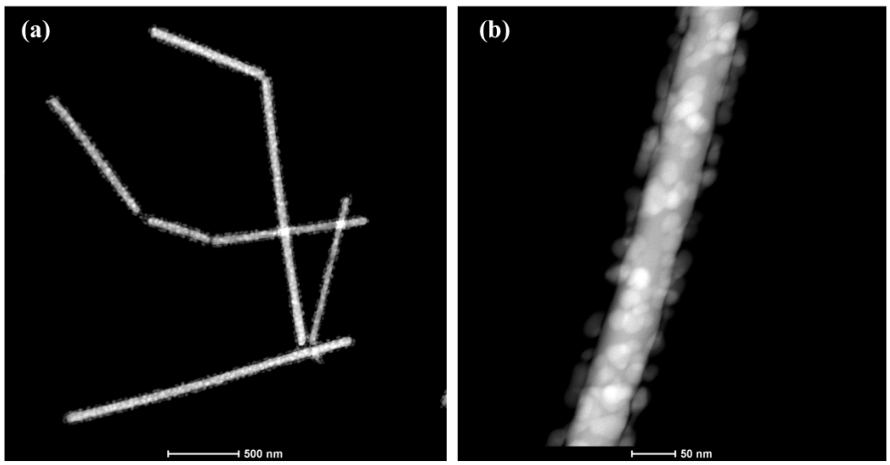


Figure 4.12. TEM images of silver nanowires exposed to solar light.

Figure 4.12 shows TEM images of a sample of silver nanowires that has been exposed to solar light for 24 hours. This images denotes the formation of nanoparticles in the surface of the silver nanowires, EDX confirms that are silver nanoparticles. This nanoparticles are produces by photoreduction due the ultraviolet light [40].

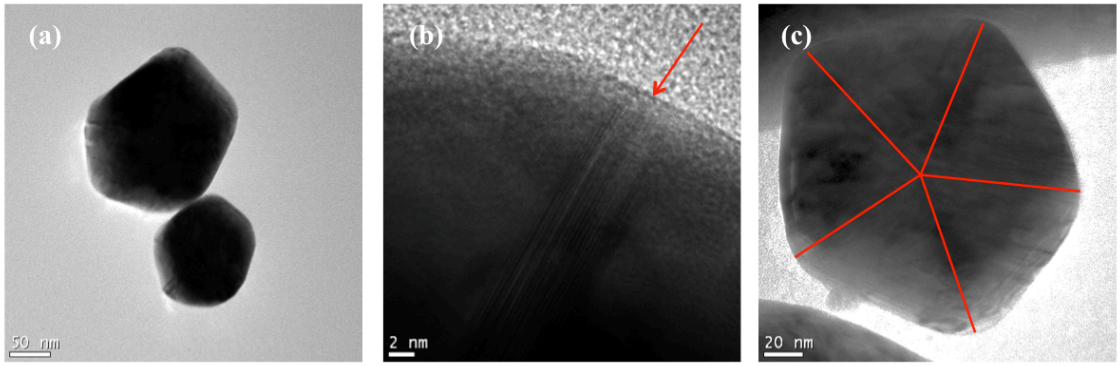


Figure 4.13. (a) TEM image of cross-section of silver nanowires, (b) and (c) HRTEM image of cross-section of silver nanowires.

Figure 4.13a shows images of the pentagonal cross-section of two silver nanowires. In Figure 4.13b, the presence of a twin can be observed. Figure 4.13c suggests that the nanowires have a multiply twinned structure as has been claimed in the literature[21,41]. Figure 4.14 shows a representation of the silver nanowire with this characteristic morphology suggested by the TEM images.

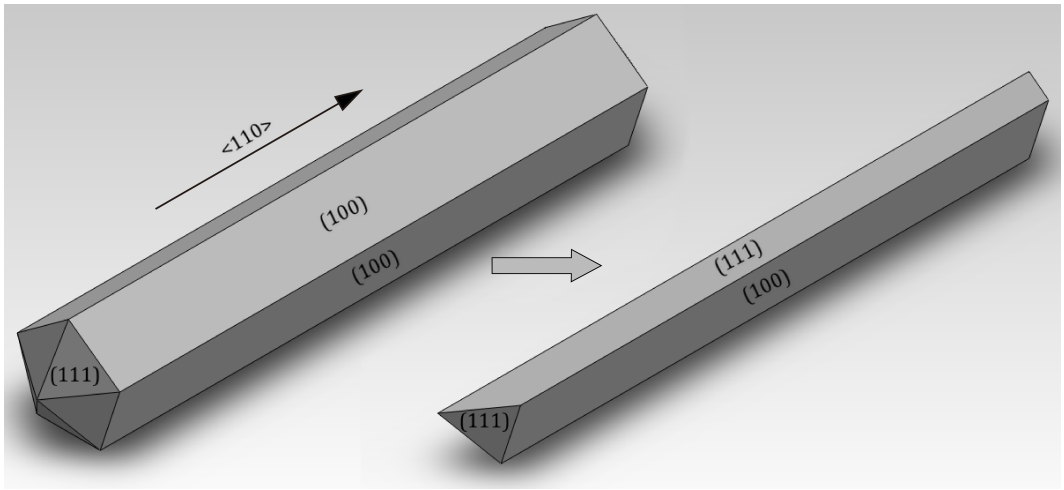


Figure 4.14. Scheme of five-fold twinned structure showing an only crystal.

According to the Gao, Y. et al [41], silver nanowires have a cyclic five-fold twinned face centered cube structure (FCC) model that is composed by 5 crystals. These crystals have {100} side surfaces and they are joined by five {111} twinned boundaries. Every crystal is twinned with its two neighbours by two {111} planes and has a {100} other face that is one of the sides of the silver nanowire. The five crystals with their five {100} faces form the entire side of silver nanowire. <110> is the axial direction of the silver nanowire. Figure 4.15 shows the correspondence of every face with their respective atomic distribution.

In the polyol method, each silver nanowire is grown from a twinned decahedral nanoparticle, where the anisotropic growth was maintained by selectively covering

{100} faces. PVP covers {100} faces leaving the {111} facets uncovered. Therefore, new silver atoms are deposited on {111} surfaces that are in the ends of the silver nanowires, which results in a 1-dimension growth of the silver nanowires. It can be concluded that PVP is vital for the nanowires synthesis.

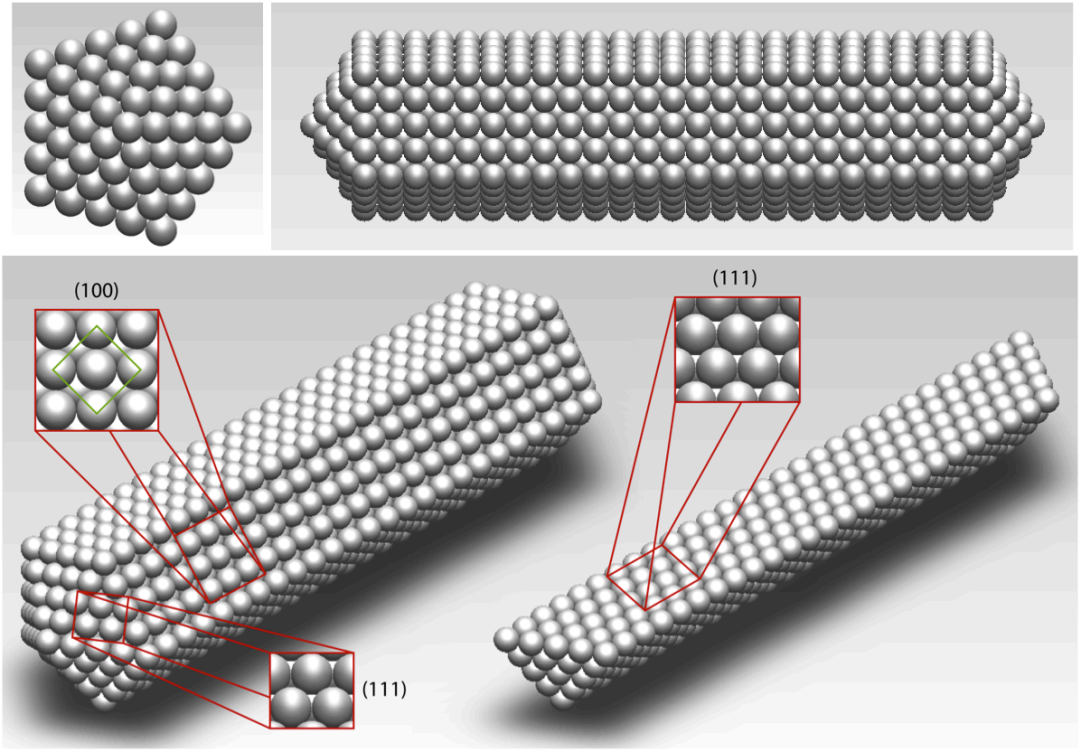


Figure 4.15. Atomic structure of a silver nanowire showing different crystallographic planes.

The five twinned crystals have a common <110> axis and the {111} facets connect them. Theoretically the angle between the crystals is 360º/5 = 72º in the silver nanowires because its pentagonal form. According to the literature, the interfacial angle between {111} lattice-twin is 70,53º. There are an offset angle of 1.47º and this generates a lattice distortion[21]. The silver nanowires have a diameter around 110 nm, the gap in the outer part of the silver nanowire can be calculated and it corresponds to 1.4 nm of distortion.

4.2.5 Selective Area Electron Diffraction

Selective Area Electron Diffraction was used in order to confirm this five-fold twinned morphology of silver nanowires. A diffraction pattern was obtained from an only nanowire. The image was obtained from a silver nanowire (Figure 4.11b) that is perpendicular to the electron beam as Figure 4.16a shows. This diffraction pattern corresponds to a sample with the following synthesis parameters: 0,1M $AgNO_3$, 0,15M PVP and 0,1mM NaCl.

In the diffraction pattern of the silver nanowire, two different networks of points can be distinguish, the green one and the orange one. Every network corresponds to a different crystal of the silver nanowire; in this case two crystals can be observed. There are several points that are in the two networks, this points are in the red line and represent the twin between the two crystals. The points of the orange network can be indexed as

belonging to the family of planes {220} that corresponds to a [111] zone axis; in the same way, the peaks of the green network belong to the families of planes {111} and {022} that corresponds to a $[1\bar{1}0]$ zone axis. Only these two crystals can be observed because these crystals are oriented so as to meets the Brag's law.

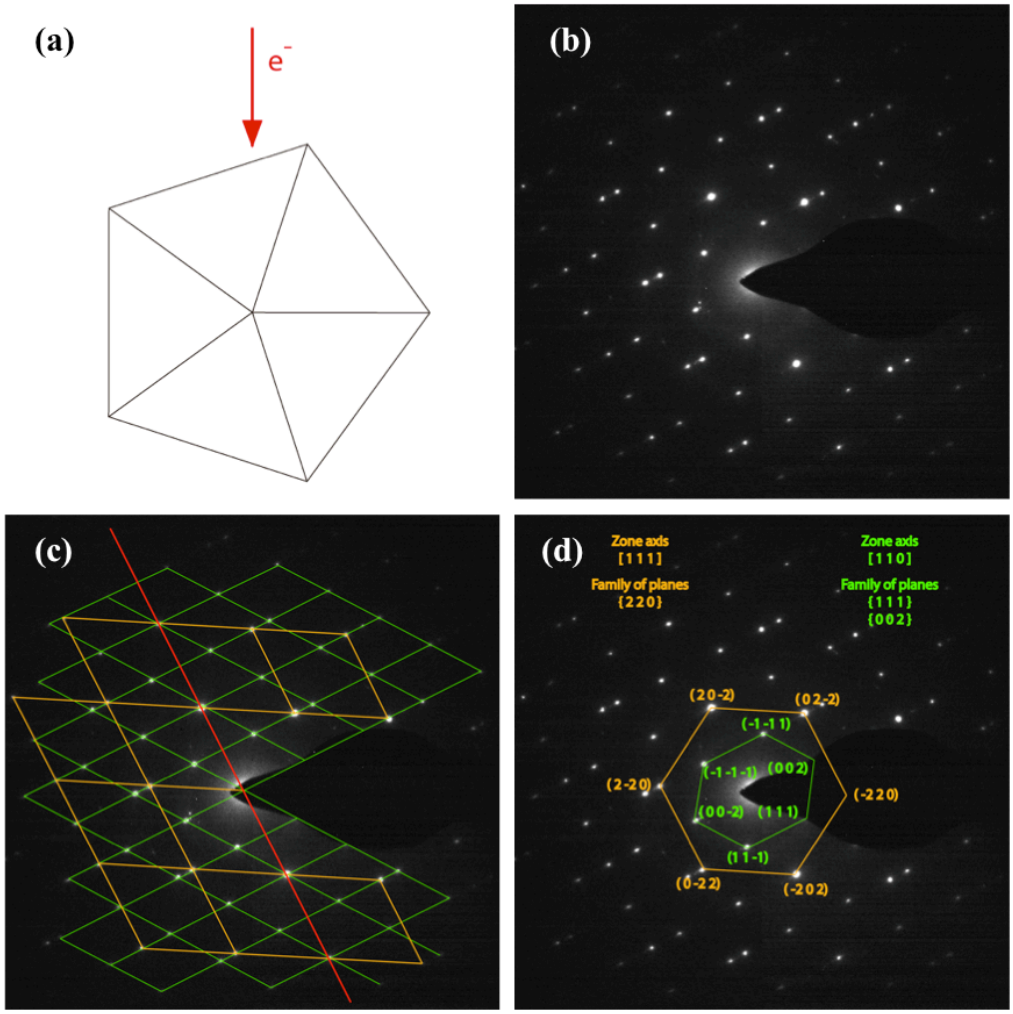


Figure 4.16. (A) Orientation of the silver nanowire and the electron beam, (b) Electron Diffraction patterns, (c) Network showing the two crystals and the twin, and (d) Indexing of diffraction points.

It can be concluded that the silver nanowires have a five-twinned structure; the advantage is that these nanowires are more conductive than polycrystalline ones. A monocrystal material has more conductivity than polycrystalline one due the absence of grain boundaries [42]. In our case, each nanowires have 5 crystals, but these crystals are arranged longitudinally. Consequently, they behave like a single crystal when the current flows along them.

4.3 Nanocomposite preparation

Nanocomposite films were prepared using two different methods: the casting evaporation method and the casting pull rod method.

4.3.1 Solubility test

The following table shows the solubility of polycarbonate in different organic solvents:

Solvent	Polycarbonate solubility (g/l)
Toluene	Not soluble
Tetrahydrofuran (THF)	65
Dichloromethane (CH_2Cl_2)	84
Chloroform ($CHCl_3$)	72

Dichloromethane is the better solvent to polycarbonate, but chloroform and tetrahydrofuran can be used as solvent because they dissolve completely the polymer too.

On the other hand, Silver nanowires can be dispersed in tetrahydrofuran and ethanol, but they have a very low dispersibility in Chloroform and dichloromethane.

4.3.2 Casting evaporation method

Casting following the first method described in the experimental section was used in a first approach to make the nanocomposite films.

Previous studies to the nanocomposite preparation denoted that Silver Nanowires were well dispersed in tetrahydrofuran and in ethanol, but have a low dispersibility in chloroform or dichloromethane. On the other hand, polycarbonate is dissolved very well by tetrahydrofuran, chloroform and dichloromethane. So tetrahydrofuran was chosen as solvent to prepare the nanocomposites.

As explained in the experimental procedure, the casting evaporation method was carried out with different methods: room temperature, ultrasonic bath and at different temperatures (60ºC and 65ºC)

Room temperature

When the solution was placed in the Petri disc, the solvent started to evaporate and when few solvent remained, the film started to form. When the solvent is finally evaporated, stress is created in the film and it crashes obtaining a non-uniform film.

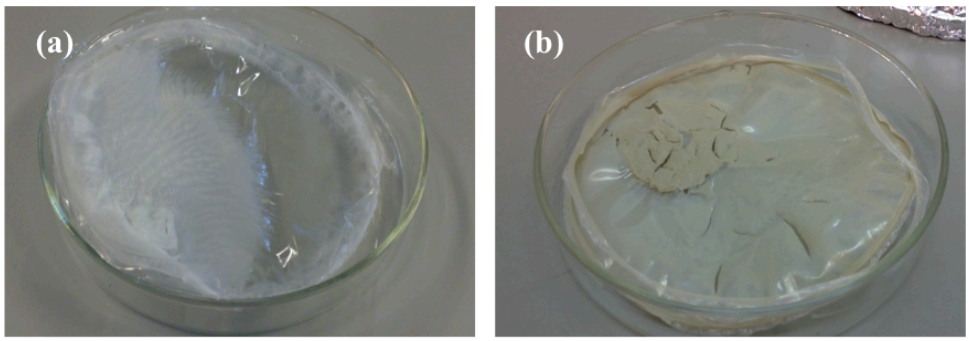


Figure 4.17. Casting of nanocomposite using THF with (b) and without (a) Silver nanowires (1%).

Figure 4.17 shows images of this very inhomogeneous films obtained by this method. The film that contain the silver nanowires have a very bad dispersion of the filler inside the polymer.

Ultrasonic bath and temperature effect

To obtain a more homogeneous composite, the Petri disc was place inside an ultrasonic bath during the evaporation of the solvent (Figure 4.18a), but the problem of the stress in the final evaporation of the solvent continued appearing.

In order to avoid this stress generated in the film, the evaporation rate was increased; the evaporation was carried out inside an oven. The boiling point of THF is 65ºC. Temperatures near the boiling point but below it to avoid the bubbling was chosen. Polymer films (without filler) at different temperatures were prepared, at 60ºC (Figure 4.18b) and 65ºC (Figure 4.18c). The stress that appears in this nanocomposite is lower than the case of room temperature, but the sample is still not very homogeneous. In addition, the sample is curved and do not have the same thickness in all the film.

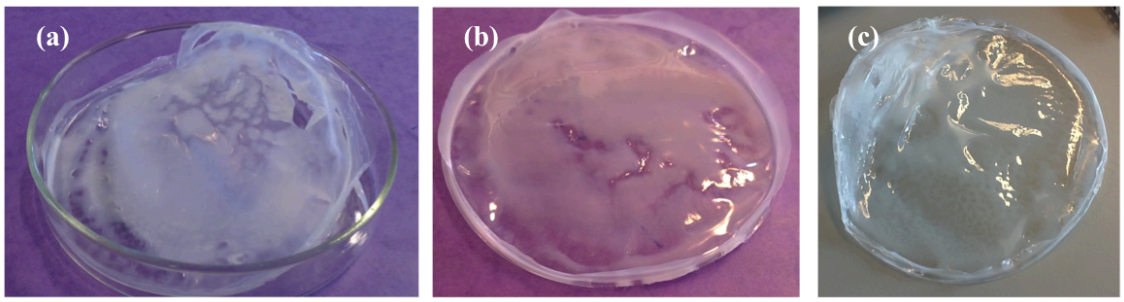


Figure 4.18. Casting of polymer using different techniques: Ultrasound bath (a), oven at 60ºC(b) and 65ºC (c).

Mixture of solvents

A casting experiment of polycarbonate without filler using dichloromethane was performed, as Figure 4.19a shows, the film was perfectly uniform and transparent, unlike the film developed using THF (Figure 4.17a). The THF as solvent is the problem for this method. However, dichloromethane cannot be used as solvent due to the low dispersion of silver nanowires in dichloromethane.

For this reason, taking advantage of the miscibility between dichloromethane and tetrahydrofuran, a mixture of solvent was purpose to solve the problem. Silver Nanowires were dispersed in THF and polycarbonate was dissolved in Dichloromethane. The two solutions were mixed, but silver nanowires started to precipitate due their low dispersibility in Dichloromethane (Figure 4.19b). Another attempt was performed using Ethanol in instead of THF, but the result was the precipitation of both silver nanowires and polycarbonate due the low solubility of polycarbonate in Ethanol.

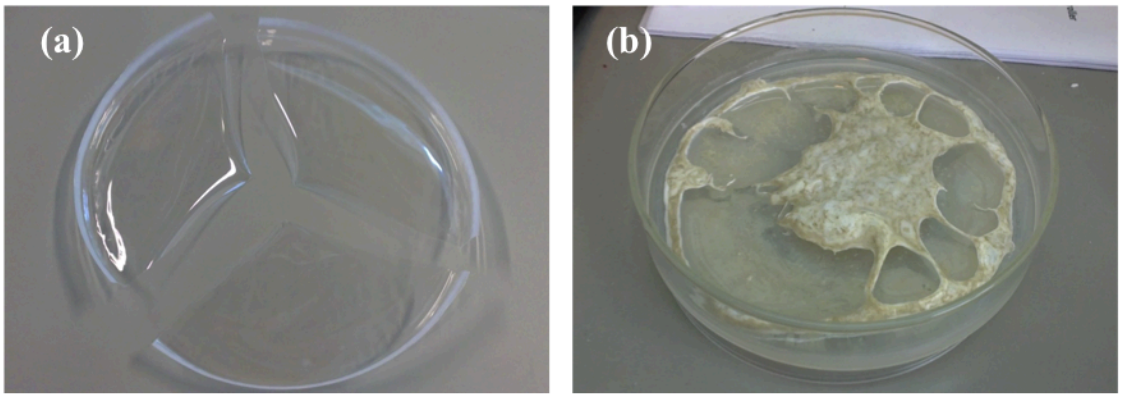


Figure 4.19. Casting of polymer using CH_2Cl_2 (a) and casting of nanocomposite with a mixture CH_2Cl_2/THF (b)

As conclusion non-uniform films were obtained by this method because when last solvent is evaporated, internal stress appear in film and it breaks down generating a rough surface film when using tetrahydrofuran. On the other hand chloroform and dichloromethane generate uniform films, but due to the low dispersibility of nanowires in these solvents the dispersion of the filler was not uniform in the films.

An alternative method was developed in order to achieve the objective and obtain uniform films using Tetrahydrofuran, the casting / pull rod method.

4.3.3 Casting / pull rod method

This method is described in the experimental section, it use a rod to drag the solution in a glass plate. With this method, stress that appears in casting is avoided because the amount of solvent that is evaporated in the glass is lower than in the previous method.

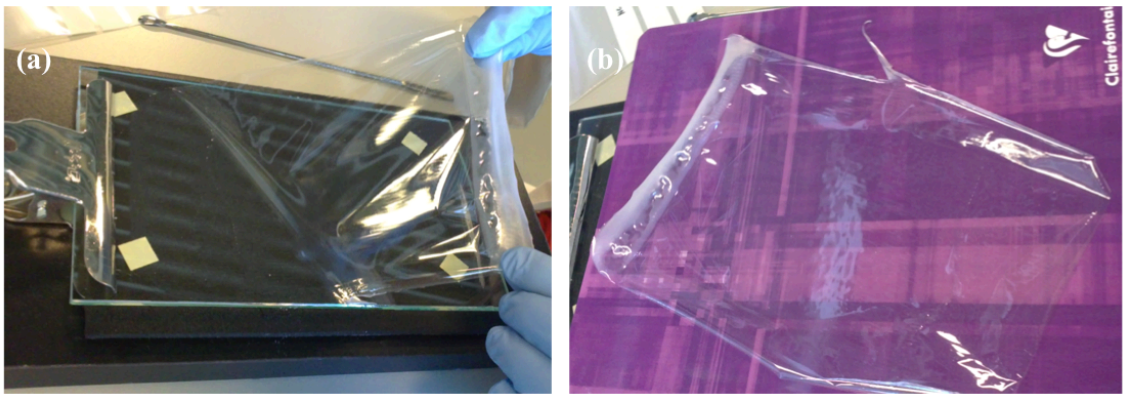


Figure 4.20. Images of the films obtained with Casting / pull rod method.

The only problem of this method was the diluted solution of the polymer that creates very thin films, around 2 μm. This films were very unwieldy due its thickness, conductivity measurement were impossible. By this reason, the evaporation step was added, in order to concentrate the solution of the polymer and then obtain a thicker film. The film thickness obtained with this method is around 20 μm.

This is the method that was chosen to prepare the nanocomposite films, and with it, we prepare nanocomposite with the following filler concentrations: Dry method (0,5wt%, 2wt% and 3wt%) and Dispersion method (0,02wt%, 0,04wt%, 0,08wt%, 0,25wt%, 0,75wt%, 1wt%, 1,5wt%, 3wt% and 4,5wt%). These methods were described in the experimental section.

4.4 Characterization of nanocomposites

These nanocomposite were characterized using TGA, SEM and Optical microscopy.

4.4.1 Thermo-gravimetric Analysis (TGA)

The theoretical concentration of the filler (silver nanowires) inside the nanocomposite is calculated previously knowing the concentration of the silver nanowires in suspension of the synthesis. This final concentration of the film is measure once the nanocomposite is made using TGA.

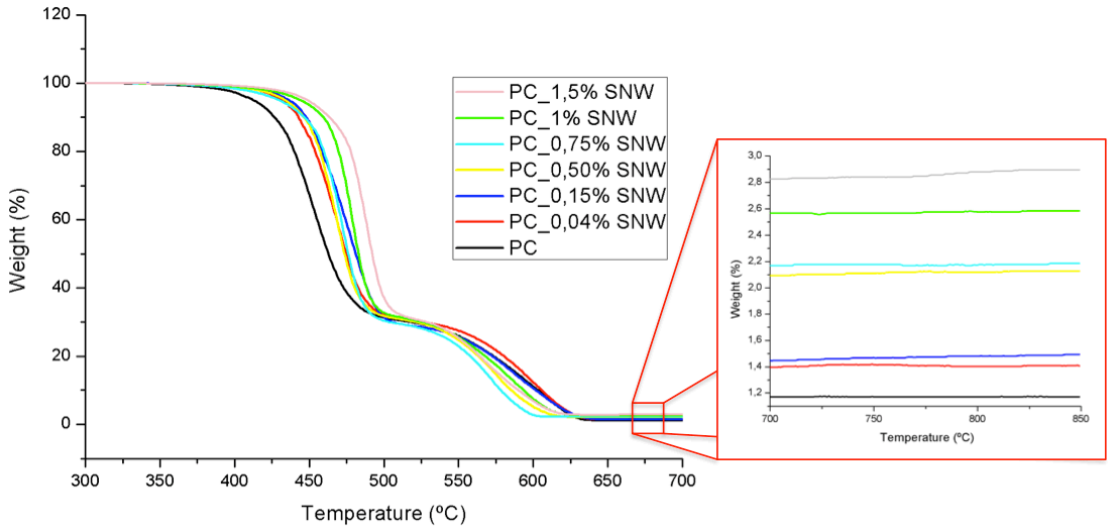


Figure 4.21. TGA measurement of nanocomposite films.

With TGA almost all the polymeric matrix is eliminated, leaving only the silver nanowires. The weight at 700ºC corresponds to silver nanowires. The theoretical filler concentration differs quite from the real concentration. This difference is due to errors in the measurement of concentration of silver nanowires.

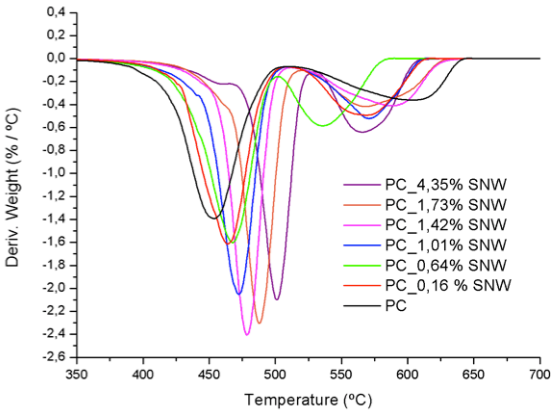
Table 4.1 shows the filler concentration of the samples that have been obtained using this methodology. From now on, all the filler concentration will be the real ones.

Two different forms to disperse the silver nanowires can be distinguished. Dry consist in drying the silver nanowires and redispersed them in THF; and dispersion consist in centrifuge the Ag NW, eliminate the solvent and redispersed the pellet in THF.

Table 4.1. Silver nanowire concentration of nanocomposite developed.

Method	Sample	Theoretical Filler (wt%)	Real Filler (wt%)
Dry	PC_0,63% SNW_DRY	0,50%	0,63%
	PC_1,35% SNW_DRY	2,00%	1,35%
	PC_2,38% SNW_DRY	3,00%	2,38%
Dispersion	PC_0,04% SNW	0,02%	0,04%
	PC_0,08% SNW	0,04%	0,08%
	PC_0,16% SNW	0,08%	0,16%
	PC_0,032 %SNW	0,15%	0,32%
	PC_0,64% SNW	0,25%	0,64%
	PC_1,01% SNW	0,75%	1,01%
	PC_1,42% SNW	1,00%	1,42%
	PC_1,73% SNW	1,50%	1,73%
	PC_2,52% SNW	3,00%	2,52%
	PC_4,25% SNW	4,50%	4,35%

Figure 4.22 shows the derivative of the weight loss curves; in the case of polycarbonate, the peak appears at 452ºC. When the silver nanowires are added to the polymer, the polymer degradation temperature increases. If the concentration of silver nanowires is increased, better thermal properties of the nanocomposite were obtained as Figure 4.21 shows, the curve shift at higher temperatures. In nanocomposite with 4,35 % of Ag NW, the curve is shifted to the right and the peak is 50ºC higher than the degradation temperature of the polymeric matrix.



Sample	Filler load (wt%)	Degradation Temperature (ºC)
PC	0%	452
PC_0,16% SNW	0,16%	464
PC_0,64% SNW	0,64%	468
PC_1,01% SNW	1,01%	472
PC_1,42% SNW	1,42%	477
PC_1,73% SNW	1,73%	488
PC_4,35%SNW	4,35%	502

Figure 4.22. DTGA measurement and table with degradation temperatures.

To conclude, silver nanowires improve the thermal properties of polycarbonate increasing the degrading temperature of the polymer.

4.4.2 Scanning electron microscopy (SEM)

Scanning electron microscopy images denote the presence of silver in the surface of the nanocomposite. Samples with different filler concentration were analyzed; 0,96% and 1,42% with dispersion method, and 1,35% with dry method samples.

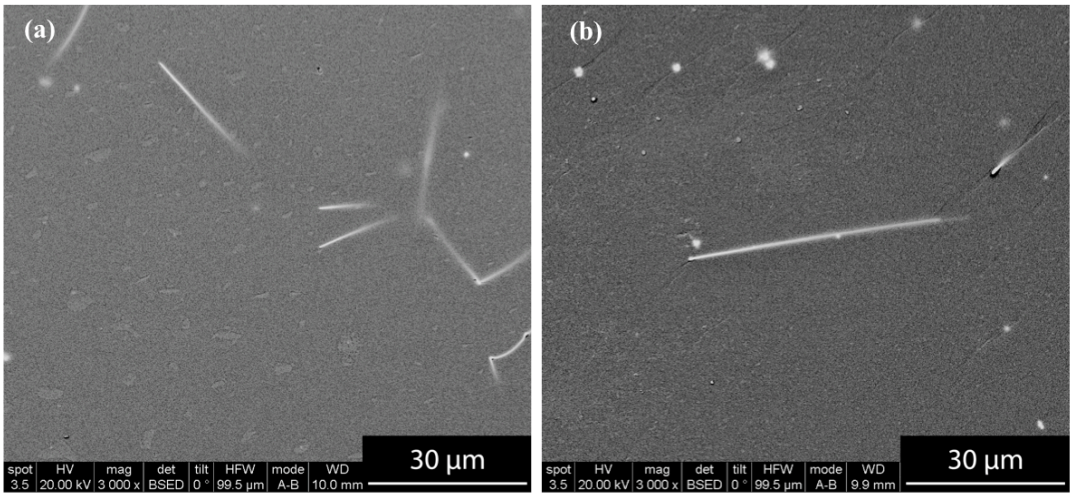


Figure 4.23. SEM images of PC_0,96% SNW.

As Figure 4.23 shows, Silver nanowires can be observed in the surface of the polymer due to backscattered electrons. In image (b), a silver nanowire that is correctly defined can be observed, due the entire nanowire is in the surface; but in Figure 4.23a, some silver nanowires that are defined in a part but then blurred and disappear. This effect is because the nanowire orientation where part of the silver nanowire is inside the polymer and other part is outside the polymer. Finally, the white points that appear in the image could corresponds to nanoparticles in the surface or nanowires that are almost embedded in the polymeric matrix but a little part of the nanowire is outside.

These nanocomposite films have been exposed to solar light. Nanoparticles in the surface of the silver nanowires do not appear in nanowires that are embedded in the polymeric matrix. This fact denotes that silver nanowires are not sensible to the ultraviolet light when they are inside the polymers.

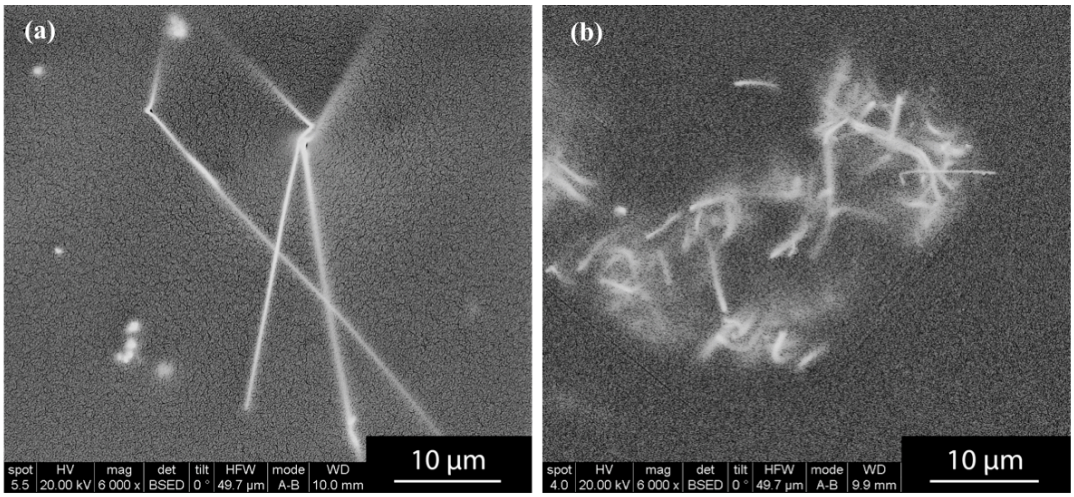


Figure 4.24. SEM images of nanocomposite using Dispersion method (a) and Dry method (b).

Figure 4.24 shows an image of a film made by Dispersion method (PC_1,42% SNW) and another made by Dry method (PC_1,35% SNW). Silver nanowires in the (b) image look like they are twisted and agglomerated forming an entire structure. In addition, these nanowires seem to be concentrated in the surface of the polymer, not inside the polymer. This effect can be produced because the silver nanowires was aggregated; they can not be dispersed in THF after drying and these aggregates do not have good interaction with the polymer. However, using the Dispersion method the silver nanowires appear very straight and they are well dispersed.

4.4.3 Optical microscopy

Optical microscopy was used in order to obtain information about the dispersion of the Ag nanowires that are inside the polymer, because SEM only provides information about the surface of the sample.

With optical microscopy, the agglomeration of silver nanowires in the Dry method is confirmed. Figure 4.25c shows an image of a film made by Dry method where the silver nanowires are agglomerated and twisted, in comparison with (d) that represent a film using Dispersion method. Image (c) corresponds to 0,63wt% and image (d) corresponds to 0,64wt% of silver nanowires.

Micrographs of the starting wires were added to the figure. As it turned out, the silver nanowires are aggregated when they are dried (Figure 4.25a). When they are redispersed in the solvent, this agglomeration is irreversible and a silver nanowires aggregates suspension is obtained, instead of the dispersed silver nanowires suspension obtained without drying as Figure 4.25b shows. To conclude, Ag nanowires must be in suspension to preserve their dispersion and their form.

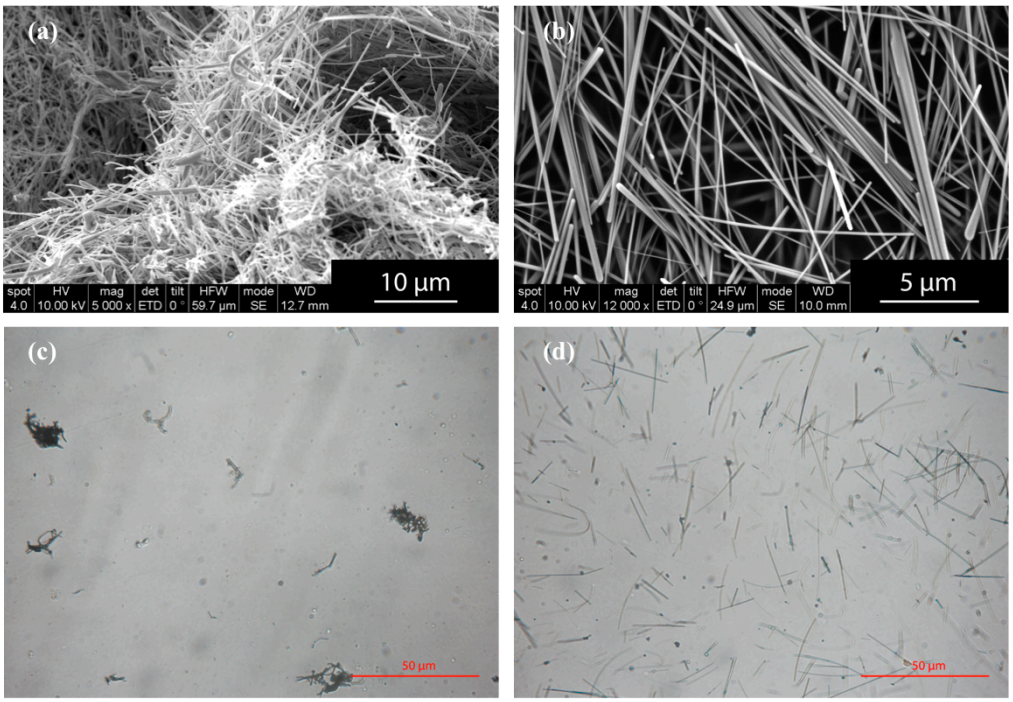


Figure 4.25. SEM images of silver nanowires dried (a) and in dispersion (b); Optical images of nanocomposite using dry 0,63% (c) and dispersion 0,64% (d) method.

This agglomeration leads to a bad dispersion of the silver nanowires inside the polymers can be seen in (Figure 4.25c). This produces an inhomogeneous polymer, undesirable characteristic for nanocomposites.

In the other hand, with dispersion method, good dispersion of the silver nanowires was obtained. They are spread in the polymeric matrix homogeneously. This would lead to a nanocomposite with uniform properties in all the material.

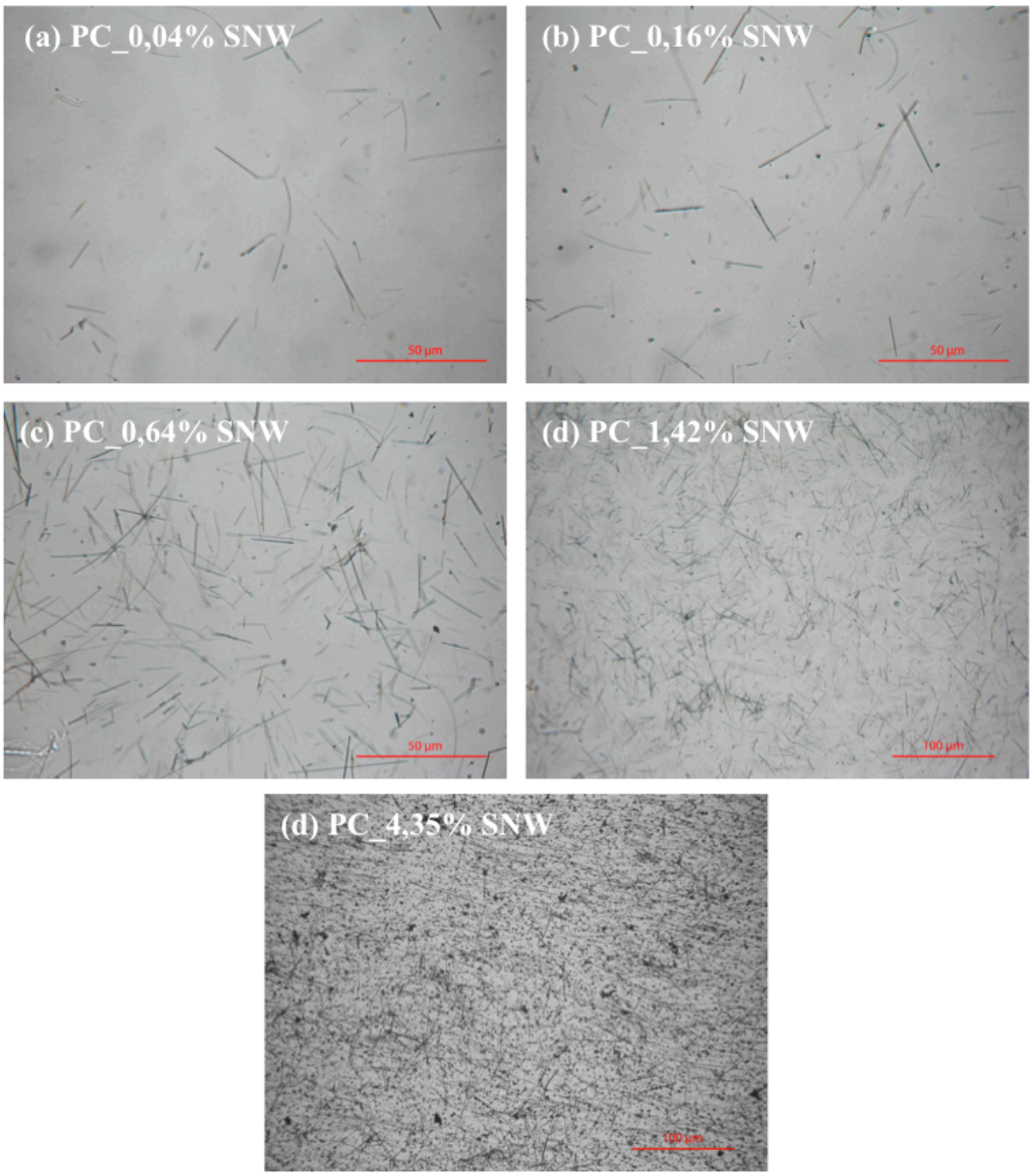


Figure 4.26. Optical images of nanocomposites with different filler concentrations.

To conclude, dispersion method is the optimal way to obtain the nanocomposite films in order to obtain a uniform dispersion of the filler inside the polymer and to preserve the properties of the silver nanowires.

In addition, optical images had been taken from films with different concentrations, as Figure 4.26 shows. Good dispersion can be observed both at high (4,35%) and low (0,04%) filler concentration.

The transparency of the films can be observed in the following pictures (Figure 4.27). Very transparent films can be observed in the case of 0,08xt% and 0,16xt% of filler. For the case of 0,64wt%, a little coloration appears. Grey coloration appears in PC_1,35%, but is a low coloration for the high filler concentration of the nanocomposite film.

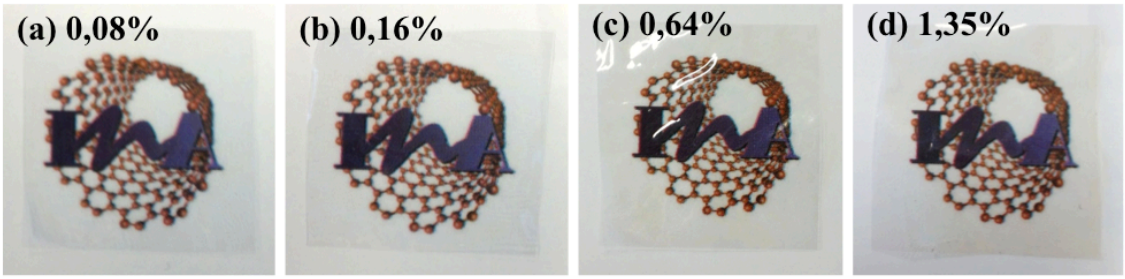


Figure 4.27. Images showing the transparency of the films.

4.5 Conductivity measurements

Conductivity of different filler concentration nanocomposite films have been measured. Samples with 0.63%, 1,35% and 2,38% filler concentration of dry casting evaporation process were measured. Samples with 0,04%, 0,08%, 0,16%, 0,64%, 1,01%, 1,42%, 1,73%, 2,52% and 4,35% filler concentration using dispersion casting evaporation process were analyzed. In addition, a polycarbonate film without silver nanowires were measured. The Nyquist and Bode curves obtained for this nanocomposite films can be analyzed in more detail. The theoretical models for the different electronic components has been developed in annex I.

Firstly, Polycarbonate films were analyzed in order to obtain information about the conductivity of the polymeric matrix.

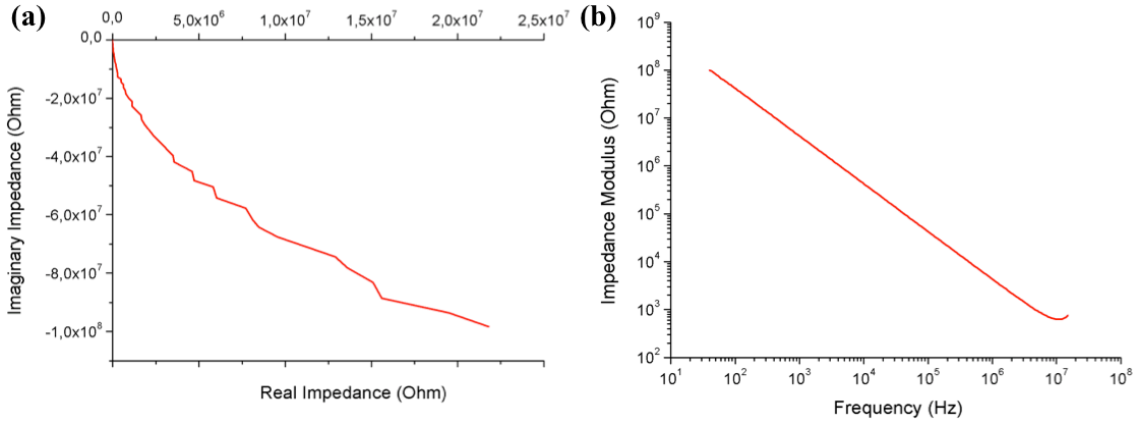


Figure 4.28. Nyquist plot and Bode plot of Polycarbonate films.

Figure 4.28a shows that Polycarbonate curve has negative values of the imaginary impedance, this denotes that Polycarbonate have a capacitive behaviour. Figure 4.28b represents the Bode curve; it has a negative slope. These results would indicate that polycarbonate film acts as a capacitor; the impedance is very high and it is known as an

insulator material. From this data, the calculated conductivity of Polycarbonate was around 5 * 10^{-11} S/cm.

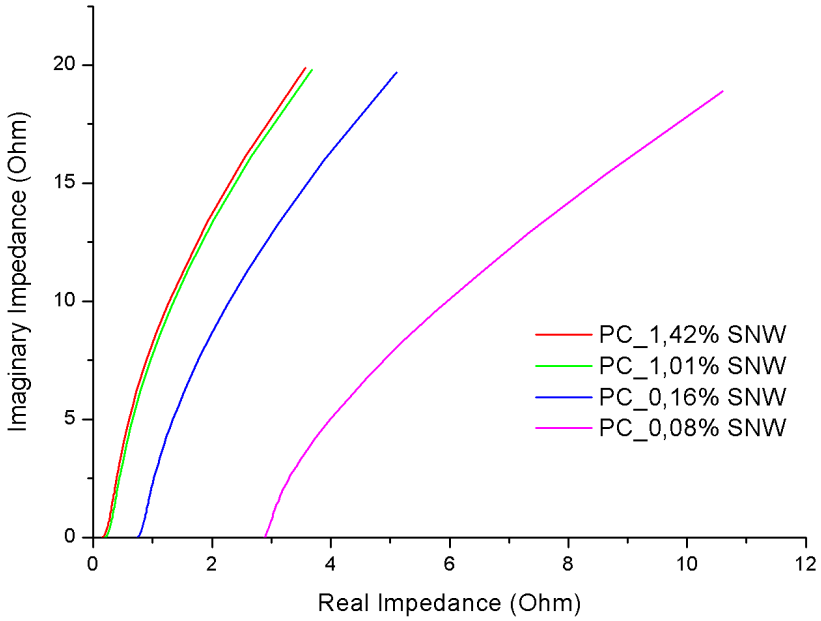


Figure 4.29. Examples of Nyquist plot of different nanocomposite films.

A different Nyquist plot (Figure 4.29) is obtained for the composite, in principle the imaginary impedance changes from negative to positive values. So when silver nanowires are added to the polymeric matrix, the behaviour of the films changes from capacitive to inductive. It can be observed that this curve corresponds to the left part of a semicircle obtained for the RL parallel association. The rest part of the semicircle is not obtained because it is out of the range of measuring of the equipment, so the points at high frequencies do not appear in the experiment. In addition, this part of the semicircle is shifted to the right, which means that in addition to the RL parallel association, a resistance is shifting the curve to the right. It can be concluded that the nanocomposite films behave as a mixed association of a Resistance-Capacitance parallel with a resistance in series.

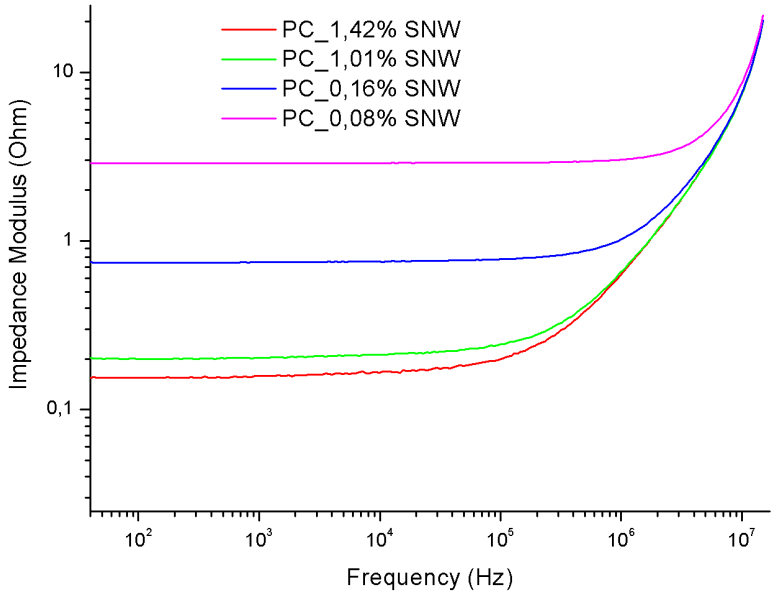


Figure 4.30. Examples of Bode plot of different nanocomposite films.

The Bode plot of the nanocomposites (Figure 4.30) confirms this fact. At low frequencies, the film behaves as a resistance and at high frequencies it has an inductive behaviour.

Conductivities of all the nanocomposite films were calculated and the average and the error were represented in Figure 4.31 versus their filler concentration. Starting from the insulating polycarbonate that has conductivity about 5 * 10^{-11} S/cm, with few silver nanowires load, conductivity increases around 7 logarithms. Looking at the graph, as the filler concentration is increased, the conductivity continues increasing until a maximum around 10^{-2} that is achieved with only 1% SNW concentration approximately.

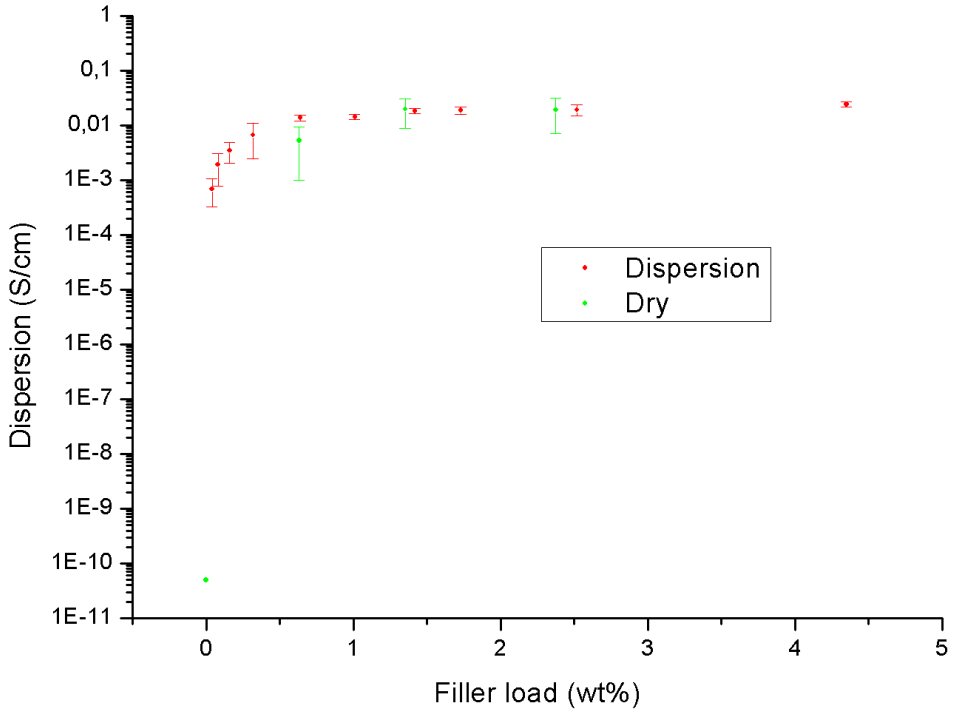


Figure 4.31. Conductivity of the different nanocomposites.

In this case, with only 0,04% of the silver nanowires concentration, the conductivity obtained is 2,99 *10^{-4} S/cm. This is a very low filler concentration, and good conductivity is obtained. In this case, the error is a larger that for the higher concentration films, but this is quite understandable considering the low concentration of Silver nanowires. This error decreases when the concentration is increased.

Petra et al [43] obtained the same conductivity (≈ 10^{-2} S/cm) in polycarbonate/carbon nanotubes composites with 1,5wt% of CNT load. It is interesting notice that with silver nanowires the percolation is around 0,08% lower than for carbon nanotubes.

For the case of Dry method films, the films present approximately the same conductivity as the Dispersion method films. But in this case, the error is significantly larger. This means that the conductivity is not the same in the entire film surface. This is due this films have a very bad dispersion and the silver nanowires were agglomerated as the optical microscope images show.

Table 4.2. Conductivity results.

Preparation method	Filler concentration (% w.t.)	Thickness (µm)	Conductivity (S/cm)
Dry	0,63%	19	$5,23 * 10^{-3}$
	1,35%	18	$1,97 * 10^{-2}$
	2,38%	20	$1,93 * 10^{-2}$
Dispersion	0,04%	18	$6,81 * 10^{-4}$
	0,08%	19	$1,91 * 10^{-3}$
	0,16%	18	$3,44 * 10^{-3}$
	0,32%	29	$6,62 * 10^{-3}$
	0,64%	18	$1,38 * 10^{-2}$
	1,01%	18	$1,42 * 10^{-2}$
	1,42%	17	$1,84 * 10^{-2}$
	1,73%	17	$1,88 * 10^{-2}$
	2,52%	18	$1,93 * 10^{-2}$
	4,35%	19	$2,42 * 10^{-2}$

Films with very high conductivity were obtained adding just a very low load of filler to an insulator polymer.

5 CONCLUSIONS

- High reproducibility synthesis of silver nanowires with a high nanowires/nanoparticles yield has been achieved using polyol solvothermal synthesis, in contrast to the polyol conventional synthesis. The yield of the wires yield is improved by the addition of NaCl, the decresase of the PVP/$AgNO_3$ ratio, washing with acetone. On the other hand, exposition to ultraviolet light produces the appearance of nanoparticles in the surface of the nanowires due photoreduction. The best precursor concentrations for the polyol solvothermal method are 0,1M $AgNO_3$, 0,15M PVP and 0,1mM NaCl.

- Nanocomposite films of silver nanowires embedded in a polycarbonate matrix were developed using casting pull rod method. Uniform thickness films (≈20 μm) have been obtained using THF as solvent. Good dispersion of silver nanowires inside the polymeric matrix has been obtained.

- High electrical conductive transparent polycarbonate films using silver nanowires as filler were obtained. Percolation was obtained at a very low filler concentration and the maximum conductivity obtained was around 10^{-2} S/cm. Besides, thermal properties of the polycarbonate were improved with the addition of silver nanowires with increase in degradation temperature of 50ºC.

6 REFERENCES

1 Zhang, W., Chen, P., Gao, Q., Zhang, Y. & Tang, Y. High-Concentration Preparation of Silver Nanowires: Restraining in Situ Nitric Acidic Etching by Steel-Assisted Polyol Method. *Chemistry of Materials* **20**, 1699-1704, doi:10.1021/cm7022554 (2008).

2 Zhu, J. J., Kan, C. X., Wan, J. G., Han, M. & Wang, G. H. High-Yield Synthesis of Uniform Ag Nanowires with High Aspect Ratios by Introducing the Long-Chain PVP in an Improved Polyol Process. *Journal of Nanomaterials* **2011** (2011).

3 Tang, X. *et al.* Rapid and high-yield synthesis of silver nanowires using air-assisted polyol method with chloride ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **338**, 33-39, doi:10.1016/j.colsurfa.2008.12.029 (2009).

4 Korte, K. E., Skrabalak, S. E. & Xia, Y. Rapid synthesis of silver nanowires through a CuCl- or CuCl2-mediated polyol process. *Journal of Materials Chemistry* **18**, 437-441 (2008).

5 Paul, D. R. & Robeson, L. M. Polymer nanotechnology: Nanocomposites. *Polymer* **49**, 3187-3204, doi:10.1016/j.polymer.2008.04.017 (2008).

6 Lee, S.-H., Teng, C.-C., Ma, C.-C. M. & Wang, I. Highly transparent and conductive thin films fabricated with nano-silver/double-walled carbon nanotube composites. *Journal of Colloid and Interface Science* **364**, 1-9, doi:10.1016/j.jcis.2011.08.029 (2011).

7 Munari, A., Ju, X., Dalton, E., Mathewson, A. & Razeeb, K. M. in *Electronic Components and Technology Conference, 2009. ECTC 2009. 59th.* 448-452.

8 White, S. I. *et al.* Electrical Percolation Behavior in Silver Nanowire–Polystyrene Composites: Simulation and Experiment. *Advanced Functional Materials* **20**, 2709-2716, doi:10.1002/adfm.201000451 (2010).

9 J., C. W. D. *Materials science and engineering. An introduction.*, (2006).

10 Gacitua, W., Ballerini, A. & Zhang, J. Polymer nanocomposites: Synthetic and natural fillers a review. *Maderas. Ciencia y tecnología* **7**, 159-178 (2005).

11 Gelves, G. A., Al-Saleh, M. H. & Sundararaj, U. Highly electrically conductive and high performance EMI shielding nanowire/polymer nanocomposites by miscible mixing and precipitation. *Journal of Materials Chemistry* **21**, 829-836 (2011).

12 P., P. K., W., S. B. & K., Y. K. Nano engineered fire resistant composite fibers. *NTC Project M02-D08* (2005).

13 Varaprasad, K. *et al.* Fabrication of silver nanocomposite films impregnated with curcumin for superior antibacterial applications. *Journal of Materials Science: Materials in Medicine* **22**, 1863-1872, doi:10.1007/s10856-011-4369-5 (2011).

14 Svoboda, P., Zeng, C., Wang, H., Lee, L. J. & Tomasko, D. L. Morphology and mechanical properties of polypropylene/organoclay nanocomposites. *Journal of Applied Polymer Science* **85**, 1562-1570, doi:10.1002/app.10789 (2002).

15 Ugucioni, J. C., Ghilardi Netto, T. & Mulato, M. Mercuric iodide composite films using polyamide, polycarbonate and polystyrene fabricated by casting. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators,*

Spectrometers, Detectors and Associated Equipment **622**, 157-163, doi:10.1016/j.nima.2010.06.257 (2010).

16 S., U. Solvent cast technology - a versatile tool for thin film production. *Colloid & Polymer Science* **130**, 1-14 (2005).

17 IAPD. in *Introduction to Plastics* (IAPD, 2003).

18 White, S. I., Vora, P. M., Kikkawa, J. M. & Winey, K. I. Resistive Switching in Bulk Silver Nanowire–Polystyrene Composites. *Advanced Functional Materials* **21**, 233-240, doi:10.1002/adfm.201001383 (2011).

19 Tang, X. & Tsuji, M. in *Nanowires science and technology* (2010).

20 Chen, D., Qiao, X., Qiu, X., Chen, J. & Jiang, R. Convenient synthesis of silver nanowires with adjustable diameters via a solvothermal method. *Journal of Colloid and Interface Science* **344**, 286-291, doi:10.1016/j.jcis.2009.12.055 (2010).

21 Zhang, S.-H. *et al.* Growth of Silver Nanowires from Solutions: A Cyclic Penta-twinned-Crystal Growth Mechanism. *The Journal of Physical Chemistry B* **109**, 9416-9421, doi:10.1021/jp0441036 (2005).

22 Sławiński, G. W. & Zamborini, F. P. Synthesis and Alignment of Silver Nanorods and Nanowires and the Formation of Pt, Pd, and Core/Shell Structures by Galvanic Exchange Directly on Surfaces. *Langmuir* **23**, 10357-10365, doi:10.1021/la701606p (2007).

23 Zhou, G. *et al.* Surfactant-assisted synthesis and characterization of silver nanorods and nanowires by an aqueous solution approach. *Journal of Crystal Growth* **289**, 255-259, doi:10.1016/j.jcrysgro.2005.11.106 (2006).

24 Nadagouda, M. N. & Varma, R. S. Green Synthesis of Ag and Pd Nanospheres, Nanowires, and Nanorods Using Vitamin B2: Catalytic Polymerisation of Aniline and Pyrrole. *Journal of Nanomaterials* **2008**, doi:10.1155/2008/782358 (2008).

25 Fievet, F., Lagier, J. P., Blin, B., Beaudoin, B. & Figlarz, M. Homogeneous and heterogeneous nucleations in the polyol process for the preparation of micron and submicron size metal particles. *Solid State Ionics* **32-33, Part 1**, 198-205, doi:10.1016/0167-2738(89)90222-1.

26 Wiley, B., Herricks, T., Sun, Y. & Xia, Y. Polyol Synthesis of Silver Nanoparticles: Use of Chloride and Oxygen to Promote the Formation of Single-Crystal, Truncated Cubes and Tetrahedrons. *Nano Letters* **4**, 1733-1739, doi:10.1021/nl048912c (2004).

27 Wiley, B., Sun, Y. & Xia, Y. Polyol Synthesis of Silver Nanostructures: Control of Product Morphology with Fe(II) or Fe(III) Species. *Langmuir* **21**, 8077-8080, doi:10.1021/la050887i (2005).

28 Jana, N. R., Gearheart, L. & Murphy, C. J. Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio. *Chemical Communications*, 617-618 (2001).

29 Tsuji, M. *et al.* Crystal Structures and Growth Mechanisms of Au@Ag Core−Shell Nanoparticles Prepared by the Microwave−Polyol Method. *Crystal Growth & Design* **6**, 1801-1807, doi:10.1021/cg060103e (2006).

30 Caswell, K. K., Bender, C. M. & Murphy, C. J. Seedless, surfactantless wet chemical synthesis of silver nanowires. *Nano Letters* **3**, 667-669 (2003).

31 Zhu, J. & Jiang, W. Fabrication of conductive metallized nanostructures from self-assembled amphiphilic triblock copolymer templates: Nanospheres, nanowires, nanorings. *Materials Chemistry and Physics* **101**, 56-62, doi:10.1016/j.matchemphys.2006.02.014 (2007).

32 Nave, R. *Impedance (HyperPhysics)*.

33 Tsuji, M. *et al.* Roles of Pt seeds and chloride anions in the preparation of silver nanorods and nanowires by microwave-polyol method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **316**, 266-277, doi:10.1016/j.colsurfa.2007.09.014 (2008).

34 Wiley, B., Sun, Y. & Xia, Y. Synthesis of Silver Nanostructures with Controlled Shapes and Properties. *Accounts of Chemical Research* **40**, 1067-1076, doi:10.1021/ar7000974 (2007).

35 Sun, Y. & Xia, Y. Mechanistic Study on the Replacement Reaction between Silver Nanostructures and Chloroauric Acid in Aqueous Medium. *Journal of the American Chemical Society* **126**, 3892-3901, doi:10.1021/ja039734c (2004).

36 Chen, D., Qiao, X., Qiu, X., Chen, J. & Jiang, R. Large-scale synthesis of silver nanowires via a solvothermal method. *Journal of Materials Science: Materials in Electronics* **22**, 6-13, doi:10.1007/s10854-010-0074-2 (2011).

37 Mastascusa, E. J. *Nyquist Plots*.

38 Xiao, C.-W. *et al.* Controlled growth of large-scale silver nanowires. *Chinese Physics* **14**, 2269 (2005).

39 Li, Z., Gu, A., Guan, M., Zhou, Q. & Shang, T. Large-scale synthesis of silver nanowires and platinum nanotubes. *Colloid & Polymer Science* **288**, 1185-1191, doi:10.1007/s00396-010-2249-z (2010).

40 Tetsumoto, T., Gotoh, Y. & Ishiwatari, T. Mechanistic studies on the formation of silver nanowires by a hydrothermal method. *Journal of Colloid and Interface Science* **362**, 267-273, doi:10.1016/j.jcis.2011.05.079 (2011).

41 Gao, Y. *et al.* Silver nanowires with five-fold symmetric cross-section. *Journal of Crystal Growth* **276**, 606-612, doi:10.1016/j.jcrysgro.2004.11.396 (2005).

42 Cho, Y. C. *et al.* Copper Better than Silver: Electrical Resistivity of the Grain-Free Single-Crystal Copper Wire. *Crystal Growth & Design* **10**, 2780-2784, doi:10.1021/cg1003808 (2010).

43 Pötschke, P., Bhattacharyya, A. R. & Janke, A. Melt mixing of polycarbonate with multiwalled carbon nanotubes: microscopic studies on the state of dispersion. *European Polymer Journal* **40**, 137-148, doi:10.1016/j.eurpolymj.2003.08.008 (2004).